NOVEL POLYIMIDE BASED INK FOR POLYJET 3D PRINTING: CHARACTERIZATION OF PRINTED MATERIAL FOR SPACE APPLICATIONS

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ABSTRACT

Additive manufacturing (AM, also known as 3D printing) is a process of material depositing, usually layer upon layer, to make objects based on a 3D computer-aided design (CAD) model. AM can be regarded as an enabling technology for future space missions. Space applications may include RF hardware, antenna components, support elements for solar panels, lightweight structures, joint elements, and electronic housings and mounts. However, before AM can be widely used in space programs, multiple challenges should be resolved first, including development of space-qualified printable materials. Development of materials and processes for space applications raise several challenges such as low mass requirement, small production series, very high performance and reliability.
PolyJet™ 3D printing works similarly to inkjet printing, but instead of jetting drops of ink in a single layer onto paper, PolyJet™ printers jet layers of liquid photopolymers on a build tray with subsequent curing by UV light. PolyJet ability to create components of great complexity and to use multiple materials simultaneously makes it useful for concept models production. Polyimides (PIs) are very attractive and widely used in space applications, however are not available in PolyJet™ technology so far.
This work presents the development of a new solvent-based PI ink. The proposed ink is the environmentally friendly solution with high solid content and low viscosity at jetting temperatures. For the first time, PI-based 3D objects were printed using Stratasys® 3D printer (Objet500 Connex™ series). The printed PI was characterized in terms of mechanical, thermal, chemical, and electrical properties.
Its durability to the space environment was confirmed by demonstrating very low outgassing, high thermal stability, and ionizing radiation resistance, as well as low dielectric constant.

INTRODUCTION

Additive manufacturing (AM) enables a new manufacturing paradigm, namely the rapid distributive manufacture of complex objects. Various types of techniques were developed based on 3D models delivered using Computer aided design (CAD) software. Models then are manufactured by depositing successive layers of liquid, powder, or sheet material, in a layer-upon-layer fashion to fabricate final 3D object. Among the most common 3D printing techniques are the fused deposition modeling (FDM) that uses thin thermoplastic filaments which are melted together; stereolithography (SLA), which forms 3D objects by illuminating the transparent bottom of a tank filled with a liquid photosensitive polymer, exposing it to ultraviolet radiation; powder bed fusion (PBF) which produces a solid part by using a thermal source (laser or e-beam) that induces fusion (sintering or melting) between the particles of plastic or metal powder one layer at a time; and PolyJet™ technology, which is similar to inkjet technology, but uses photosensitive polymer droplets, cured to form a solid layer prior to addition of the next on-top layer [1, 2]. PolyJet™ 3D printing technique enables achieving extremely smooth surfaces and complex geometrical structures with high precision. Another great advantage of the PolyJet™ printing is its ability to use a few materials in a single prototype which is often referred to as digital materials. Digital materials can have different mechanical properties and they can be multi-colored as well [3-5].
AM is well-suited for space applications: it is adaptive to very small series, applicable to dimensions ranging from few micrometers to meters, applicable to a wide variety of materials (polymers, metals, ceramics, composites, etc.), allows for complex geometry that could not be manufactured otherwise, enables reduction of interfaces, provides performance improvement, shortens lead times, minimizes material waste, and could be used for spacecraft construction and even for on-orbit manufacturing. Thus, AM can be regarded as an enabling technology for future space missions [1]. Space applications may include RF hardware, antenna components, support elements for solar panels, lightweight structures, joint elements, and electronic housings and mounts. However, before AM can be widely used in space programs, multiple challenges should be resolved first, including development of space-qualified engineering printable polymers with desired characteristics.

Engineering polymers are materials with superior thermal stability and mechanical properties that makes them valuable for the manufacturing of structural components. Examples of engineering polymers include epoxy resins, polyurethanes, polyamides, polyacrylates, polycarbonates, polyesters, and polyimides (PIs). PIs are very promising due to the variety of desirable characteristics they possess, including high thermal stability, excellent mechanical properties, wear resistance, radiation resistance, suitable thermo-optical properties, inertness to solvents, low dielectric constant, and good adhesion strengths [6-8]. They are widely used in space applications, e.g. as multilayer thermal blankets (MLI), as flexible and/or rigid extendable structures, as low k dielectric materials in electronic devices and circuit boards [9].

The reputation of the PIs has been established based on outstanding properties and versatility unparalleled in most other classes of macromolecules. The goal of our research is the fabrication of the PI-based structures by PolyJet™ 3D printing. Current PolyJet™ technology offers the capability to use a range of polymeric materials with a variety of properties. Common printable polymers [3, 10] are mostly thermoplastic polymers such as Polypropylene, High-density (HD) Polyethylene, acrylonitrile butadiene styrene (ABS), Polyphenylsulfone (PPSU), or high impact polystyrene (HIPS). However, engineering polymers, especially PIs are not currently used as inks in PolyJet™ AM.

The PolyJet™ process requires strict ink characteristics, dictated by the inkjet print-head (PH) design. Proper jetting is determined by the Ohnesorge number which combines the viscosity, density and surface tension of the liquid [11]. Among these properties, the surface tension and viscosity are the most crucial. Typical surface tension of the ink should fall within the range 28 – 32 mN/m and the required viscosity should be 14-20 cPs at jetting temperature. Another critical consideration in the development of ink formulation is the ability to cure and solidify the wet film instantaneously, preferably by UV radiation.

The main obstacles in applying PIs in a PolyJet™ 3D printing technology are: (i) slow curing kinetics accompanied by release of the low-molecular weight product (water); (ii) very low solid content limiting the printing process; (iii) the use of high boiling point toxic solvents; (iv) the need for imidization and curing processes at elevated temperatures in the range of 150ºC - 350ºC; (v) the need to remove large amount of solvent.

Recent research demonstrated inkjet printing of PIs by jetting polyamic acid solutions, followed by thermal imidization [12]. F. Zhang et al., claim to print 3D insulators using the same approach of polyamic acid condensation, however the Z-dimension of these structures was below 1 μm [13]. Though PI-based inks were proposed before, their long curing time (10-60 min) does not enable their use in PolyJet™ process [14]. In a different study, Guo et al. reported preparation of a solvent free photo-curable PI ink. However, the viscosity of this ink was very high and not suitable for PolyJet technology [15].

Our work suggests Bismaleimides (BMIs) as the most promising precursor for PI inks formulation. BMIs [16, 17] are type of PIs used for preparation of thermosetting materials. They consist of imide moieties in low molecular weight pre-polymers that have reactive terminal or pendant groups, which undergo homo- and/or copolymerization by thermal or catalytic means [8]. Such materials are characterized by relative ease of processing and the ability to tailor specific rheological properties by controlling the molecular weight. Additionally, crosslinked thermosetting PIs have excellent retention of physical properties at high temperatures, in wet environments, and in the presence of solvents and lubricating fluids. Although thermal curing is currently the most widely used method for curing BMI, UV curing has been investigated [18] as a technique that possesses many advantages, such as room temperature (RT) cure, high reaction rate, energy efficiency, low volatility of organic compound, and ease of control. However, BMI resins are mostly solid or high viscous at RT and hence cannot be ink jetted. Viscosity reduction can be achieved by dilution with an appropriate solvent and/or heating to elevated temperature.

This work presents the development of a new solvent-based PI ink [19]. The developed ink is an environmentally friendly solution with high solid content and low viscosity at jetting temperature. For the first time, PI-based 3D objects were printed using ink-jet printer, Stratasys® Objet500 Connex™ series. The printed PI was characterized in terms of thermal, mechanical, chemical, and electrical properties. Its durability to the space environment was confirmed by demonstrating very low outgassing, ionizing radiation resistance, low dielectric constant, and high thermal stability.

Novel PI inks were successfully printed by cirp GmbH using PolyJet technology, showing a potential for a scale-up and commercialization of these materials [20].

2 EXPERIMENTAL

2.1 Ink preparation

PI-based inks were prepared from commercially available BMI monomers (Designer Molecules Inc). One of the most suitable monomers, used in this work, is BMI 689, which contains a non-hydrogenated dimer diamine backbone, as presented in Fig. 1. Irgacure 819, from BASF Dispersions & Pigments, and TPO-L (by SpeedCure) were added as photoinitiators for radical polymerization of the BMI precursor upon UV light exposure. Reference BMI films were thermally cured using a thermal initiator, dicumyl peroxide (98%, Sigma Aldrich).

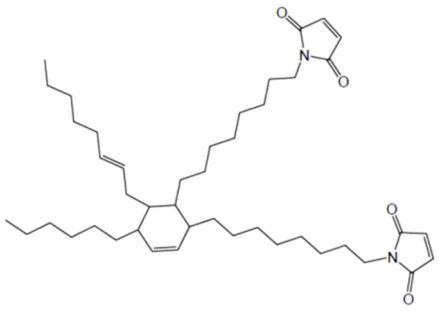

Fig. 1. Representative structure of BMI 689 (Designer Molecules Inc.) [21].

BMI-based solutions were prepared by mixing BMI precursor in different solvents, such as butyl acetate and hexyl acetate, from Sigma Aldrich. Vortex mixer (Velp. Scientifica, ZX classic), and sonicator (Kudus, SK221OHP) were used to prepare homogeneous solutions. Solubility of the photoinitiators was achieved by a proper solution heating.

2.2 Curing and printing of the PI ink

Planar BMI-based films were thermally cured in aluminum molds on a hot plate-based oven in a N_2 atmosphere. The films were easily released from the molds due to pre-spreading of Watershield™ release coating (Zyvax Inc.) on the mold surface. Samples for mechanical properties investigation were casted using 3mm × 20mm aluminum molds.
UV curing of BMI films directly from solution was enabled using a LED lamp, FJ200 of Phoseon, 20 W/cm^2 at 385 nm. Some of the films were post-cured by UV mercury lamp (EXFO, OmniCure S1000) with power density of 0.06 W/cm^2, as detected by Ophir detector FL400A-BB-50 and power meter (Nova II, Ophir).
The printing of 3D models was performed on Stratasys® Objet500 Connex™ series 3D printer, equipped with Ricoh E1 PH, thermoregulated printing tray, and Ceramic Infrared Heater (500 W, model T-HTS/2, Elstein). The printing trials were performed in a single jetting mode, with layer thickness of about 30 µm. Part of the samples were printed using Ricoh Gen4L PH.

2.3 Characterization techniques

The viscosity of the developed ink was measured by Rolling-ball viscometer (Lovis 2000 M/ME, Anton Paar) with thermoregulation by water circulation (F12, Julabo). The surface tension was measured by Sigma Force Tensiometer, model 700/701, by Biolin Scientific, using the du Noüy ring method.
Thermogravimetric analysis (TGA) was carried out using a TGA 550, by TA Instruments, with a heating rate of 5°C/min up to 400°C in N_2 atmosphere.
The mechanical properties of the casted and printed films were derived from stress-strain curves obtained by dynamic mechanical analysis (Q800 DMA of TA Instruments) under 3-point bending. Stress vs. strain tests were performed using a 5 mm wide 3-point bending grip at 30°C, pre-load force of 0.01 N, at a rate of 0.5 N/min.
FTIR measurements were carried out using a NICOLET iS10 FTIR, in iD5 ATR-Diamond mode.
Outgassing tests were carried out in accordance with the ASTM E595 standard to determine total mass loss (TML), collected volatile condensable material (CVCM), and water vapor regain (WVR) values [22]. The samples were weighed before and after the outgassing test with a precision of ± 0.1 µg. The vacuum system, equipped with a dry turbo-molecular pump, ensured a base pressure lower than 1×10^{-5} Torr. The hot module of the system, which contained the samples, was maintained at 125±1ºC and the cold module onto which the collectors were installed, had a temperature of 25±1ºC, as required by the ASTM E595 standard. Upon the outgassing test completion, WVR values were determined by placing the samples into a humidity cell (50±5 % relative humidity) for 24 hours and weighing them thereafter.
The effect of ionizing radiation on the structure and mechanical properties of the printed samples was tested by exposure to γ radiation. Samples were exposed to 0.5 Mrad and 1 Mrad γ radiation doses, using a ^{60}Co source (Gamma cell 220 type B from Nordion International Inc.), with spectral peaks at 1.33 MeV and 1.17 MeV) in ambient pressure at RT. The dose rate was about 3.0 krad/h.

3 RESULTS

A comprehensive work has been performed on the development of the PI ink that included selection of the BMI precursor and solvent, characterization of the ink physical properties, studies of the curing behavior, and optimization of the jetting and printing conditions. In this paper we describe (i) the properties of ink formulation, optimized for jetting and printing by Objet500 Connex™ series 3D printer using Ricoh E1 PH. This formulation consists of 80 wt.% BMI-689 in hexyl acetate and a mixture of photoinitiators; (ii) the printed material properties including thermal and chemical stability, outgassing properties, ionizing radiation effect, and dielectric properties.

3.1 Ink characterization

The physical properties of the developed ink were measured as they are crucial for jetting and printing conditions. The viscosity of the ink, measured as a function of temperature, is shown in Fig. 2 in the RT to 60°C temperature range.
The viscosity is a logarithmic function of reciprocal temperature, and hence viscosity values at relevant working range can be found by extrapolation, as shown

in Fig. 2b. It was observed that the temperatures between 68 and 72°C provided the desired jetting viscosity of 14-16 cP. We selected 68°C as the satisfactory test jetting temperature.

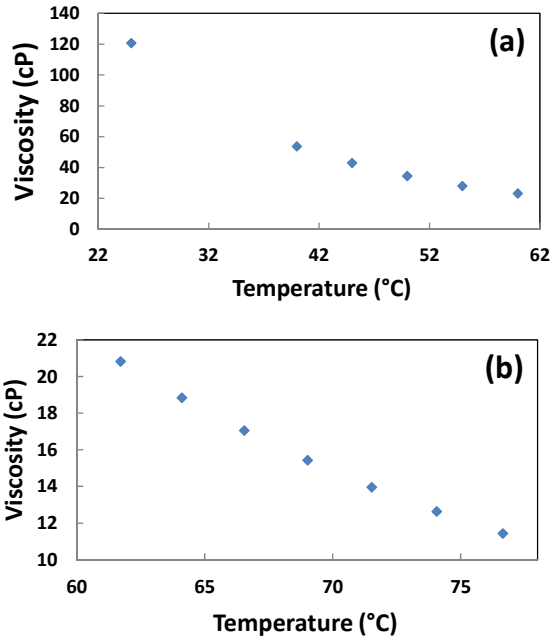

Fig. 2. Viscosity of PI-based ink as function of temperature: (a) measured values, (b) extrapolated to relevant working range.

The surface tension influences the wetting of the ink on the orifice plate. According to the lattice Boltzmann-based binary fluid model for inkjet printing, higher surface tension values promote earlier droplet breakup and faster drop velocity. Therefore, using inks with high surface tensions will improve the printing quality [23]. Fig. 3 shows the static surface tension of the PI-ink as a function of temperature in the RT – 55°C range. Linear correlation of the surface tension with temperature allows to determine the characteristic value at higher temperatures by extrapolation. The surface tension at 68°C (jetting temperature) was calculated as 28.56 mN/m. The obtained surface tension suffices the jetting requirements.

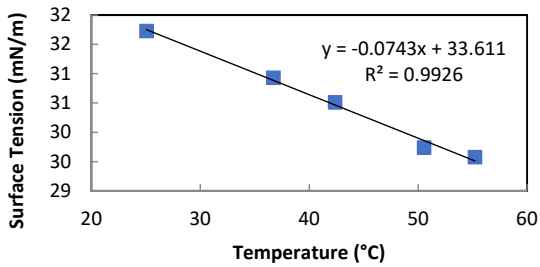

Fig. 3. Static surface tension of PI-based ink at different temperatures, as measured by a Force Tensiometer.

3.3 Characterization of the printed material

Various 2D-like and 3D model structures were printed using either Ricoh E1, or Gen4L PHs. They include 1.5 mm - thick "dog bone" samples, 300 µm thin films, and 1 cm - height pyramid, as shown in Fig. 4. These structures were used for optimization of printing parameters, studies of the material properties, and optimization of post curing conditions. It must be emphasized that the pyramid samples are the first 3D PI objects printed by PolyJet™ technology. Fig. 4c shows sharp edges and relatively smooth surface of these objects.

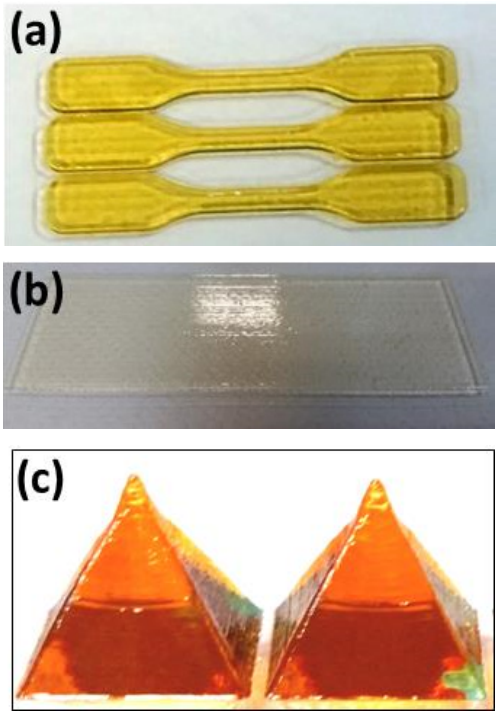

Fig. 4. 2D-like and 3D printed PI samples: (a) 1.5 mm thick – "dog bone"; (b) 300 µm – thick film; (c) 1 cm – height pyramid

3.3.1. Thermal stability

The thermal stability of printed PI samples was measured by TGA before and after post curing. The PI samples were printed using Objet500 printer and Ricoh E1 PH at 68°C, while the printer tray was heated to 60°C. The printed sample is composed of 9 slices, each slice deposition was followed by 10 scans of two Hg lamps and single IR ceramic lamp at 880°C. The post curing was carried out for 60 min at 275°C in N_2 atmosphere. The mass loss of as printed samples and samples after post curing was measured by TGA. The accuracy of the measurement is about 10%. The average data from 3 independent measurements are shown in Table I and in Fig. 5. The results indicate that thermal stability improves significantly after post curing: a mass loss of 1 wt.% was observed at 165°C and at 270°C for

as-printed and post cured samples, respectively.

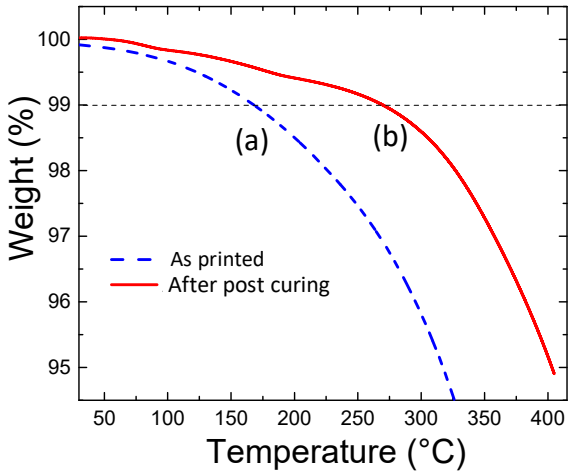

Fig. 5. TGA measurements (5°C/min in N_2 atmosphere) of printed PI: (a) without post curing; (b) after post curing for 60 min at 275°C.

Table I. Weight loss as a function of temperature, measured by TGA for as-printed and post cured samples.

Temp. (°C) / Weight loss (%)	As-printed	Post-cured
1	165	270
2	225	325
3	265	360
5	315	400

3.3.2. Chemical stability

Casted and UV cured PI films, without additional thermal post treatment, were used for testing of chemical resistance. The material was tested for stability in tetrahydrofuran (THF), 2,4,6-trichlorobenzene (TCB) and N-methyl-pyrrolidone (NMP). Fully cross-linked films show good resistivity against these harsh solvents. The tests were carried out at RT and at 40°C in an ultrasonic bath. The samples were exposed to different solvents for 30 - 90 min following by solvent evaporation and the measurements of the weight loss. In all tests no measurable weight loss or weight gain was observed.

3.3.3. Outgassing properties

Outgassing tests were carried out for casted and thermally cured PI samples, and for printed samples after post curing. Thermal curing was performed for 30 minutes at 150°C, followed by 60 minutes at 250°C or 300°C. Printed PI samples were post-cured for 60 min. at 275°C. Table II summarizes standard TML, CVCM, and WVR values for the tested samples. The outgassing criteria for space qualification are TML ≤ 1% and CVCM ≤ 0.1% according to ASTM E595 [22]. WVR is measured as an indication of water adsorption.

Table II. Standard outgassing parameters of casted and printed PI materials.

Sample type/ Curing	TML (%)	WVR (%)	CVCM (%)
Casted, 30 min, 150°C + 60 min. 250°C	0.148	0.147	0.003
Casted, 30 min, 150°C + 60 min. 300°C	0.184	0.151	0.001
Printed, post-cured 60 min. 275°C	0.241	0.190	0.008

It can be seen that both printed and casted samples have TML and CVCM values well below 1.0 % and 0.1 %, respectively. The results indicate that the material is space qualified, regarding outgassing properties, and that the contamination risk induced by this material is very low. It is particularly important to note negligible values of CVCM, which makes these materials qualified for applications in the vicinity of contamination sensitive optical systems. Moreover, low values of WVR indicate especially low humidity absorption. This characteristic is important in applications where dimensional stability is under concern. The overall outgassing properties of the developed PI-based material are better than that typically observed for Kapton® films: TML ~ 0.8-1.0%, CVCM ~ 0.0-0.2%, WVR ~ 0.8-0.9% [24].

3.3.4. Ionizing radiation

Printed samples after post curing for 60 min at 275°C were subjected to 0.5 Mrad and 1 Mrad γ radiation in order to simulate the effect of ionizing radiation typical for external spacecraft surface at Low Earth Orbit (LEO) for about 5 years. No visual changes were observed after exposure to both radiation doses, as shown in Fig. 6.

Typical 3-point bending stress-strain curves measured for unexposed and exposed samples are shown in Fig. 7; the mechanical properties that were obtained from these measurements are summarized in Table III. It can be seen, that the samples became more brittle after exposure to higher radiation doses, as indicated by the decrease in the strain at break values and increase in the elastic modulus, most likely due to additional cross-linking created by the ionizing radiation [25]. However, the stress at break values were not affected by the γ radiation.

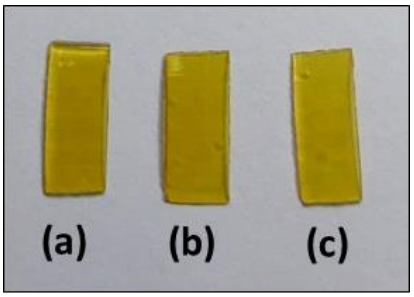

Fig. 6. Images of the printed samples with post curing for 60 min at 275°C in N_2 atmosphere before and after exposure to γ radiation: (a) unexposed, (b) 500 krad, (c) 1000 krad.

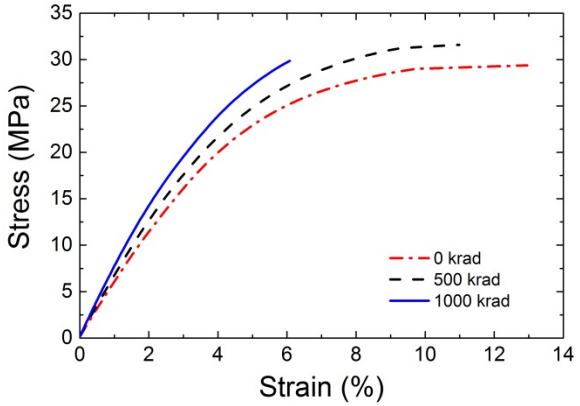

Fig. 7. Typical 3-point bending stress-strain curves of printed samples with post curing for 60 min at 275°C in N_2 atmosphere before and after exposure to γ radiation.

Table III. Averaged stress at break, strain at break and elastic modulus of printed samples after exposure to various doses of ionizing radiation

Radiation dose (krad)	Stress at break (MPa)	Strain at break (%)	Elastic modulus (MPa)
0	29.8±1.1	11.2±1.5	631.2±36.9
500	31.1±2.7	10.9±1.1	720.1±34.3
1000	31.6±1.8	6.9±0.8	780.2±60.4

FTIR measurements were performed in order to get more insight into the radiation-induced changes of the chemical structure. Fig. 8 shows FTIR spectra in the transmittance mode for unexposed and irradiated samples. The bands at 2920 cm^{-1} and 2850 cm^{-1} represent C-H vibrations, the band at 1700 cm^{-1} corresponds to the carbonyl groups of the terminal maleimide. The absence of the bands at 825 cm^{-1} and 695 cm^{-1}, characteristic for the C=C double bonds, indicate a full curing of the BMI precursor. The exposure to γ radiation does not affect the FTIR spectrum significantly. A slight decrease is seen in the C-H and C=O vibrations, which might be an indication of a maleimide ring opening. The opening of the maleimide ring by radical mechanism is, most likely, followed by secondary radical reactions. These reactions lead to a formation of a more rigid tree-dimensional thermoset structure, in accordance with the changes in mechanical properties.

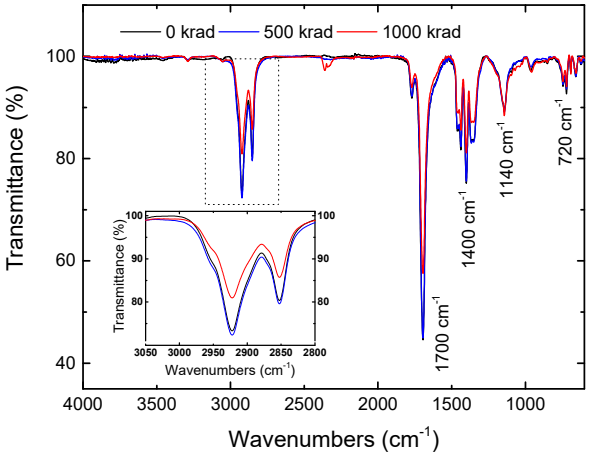

Fig. 8. FTIR measurements of printed samples (post cured for 60 min at 275°C in N_2 atmosphere) before and after exposure to γ radiation: unexposed (black); after 500 krad (blue) and after 1000 krad (red) radiation dose.

3.3.5. Dielectric constant measurements

The dielectric constant of casted and printed PI film was measured and compared to that of commercial Kapton® film (125µm). Square gold electrodes were deposited by e-beam evaporator on the surface of the PI film samples. The capacitance of the films was measured using Agilent U1733C, ZLCR. The dielectric constant, ε_r, was calculated from the following equation:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d},$$

where ε_0 is the vacuum dielectric constant, 8.85 10^{-12} F/m, A is the area of the PI capacitor, and d is its thickness. Table IV shows the average (out of three samples) dielectric constant for each type of PI film. It is observed that the dielectric constant of the developed PI material is close to that of the commercial PI, Kapton®.

Table IV. The dielectric constant of different PI films.

Sample	Dielectric constant
Kapton® 125µm	3.38
Casted material	3.43
Printed material	3.29

CONCLUSIONS

Additive Manufacturing is a relatively new technology which can be exploited for various novel space applications. However, most current printable materials will not endure the space environment. In the present work we demonstrate a development of PI ink that can be used in 3D printing of space qualified components. The innovative PI ink solution is characterized by low viscosity, high solid content, it is environmentally friendly, and it is suitable for PolyJet™ 3D printing technology. 2D-like and 3D PI objects were printed for the first time by Inkjet technology which allows extremely smooth surfaces, complex geometrical structures, and high precision. The printed material shows superior properties that are specifically suitable for space applications: low outgassing, high thermal stability, low water absorption, high radiation stability, and low dielectric constant. The obtained properties of the printed PI material open a wide range of potential applications in space technology and electronics.

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