

Full Length Article

Effect of ionising radiation on the mechanical and structural properties of 3D printed plastics

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ABSTRACT

This work investigates the evolution of the tensile and structural properties of fused filament fabrication (FFF), formed polymers under gamma irradiation. Commercial off-the-shelf print filaments of Poly(lactic acid) (PLA), Thermoplastic polyurethane (TPU), Chlorinated polyethylene elastomer (CPE), Nylon, Acrylonitrile butadiene styrene (ABS) and Polycarbonate (PC) were exposed to gamma-ray doses of up to 5.3 MGy. The suitability of FFF-formed components made from these materials for use in radiation environments is evaluated by considering their structural properties. We identify clear trends in the structural properties of all the materials tested and correlate them with changes in the chemical structure. We find that Nylon shows the best performance under these conditions, with no change in ultimate tensile strength and an increase in stiffness. However, some of our findings suggest that the effect of additives to this type of filament may result in potentially undesirable adhesive properties. The organic polymer PLA was notably more radiation-sensitive than the other materials tested, showing 50% decrease in Young's Modulus and ultimate tensile strength at order of magnitude lower radiation dose. A mechanism is proposed whereby FFF-processed components would have substantially different radiation tolerances than bulk material.

1. Introduction

Components formed by fused filament fabrication (FFF) have potential applications in radiation environments. To date, an in-depth analysis of these material's tensile properties in such an environment has not been performed; to the best of our knowledge, there is one published study addressing this topic at up to 1.5 MGy, Ref. [1], and two others at 10–200 kGy dose levels, Ref. [2,3]. Another article has studied radiation damage to 3D structures produced by Direct Ink Wetting (DIW) [4]. Our work provides an extension to these studies by performing tensile tests on a range of popular off-the-shelf print filaments (PLA, ABS, Nylon, TPU, PC, CPE and CPE+) exposed to gamma radiation up to 5.3 MGy.

In recent years, mechanical testing of 3D printed materials [5–7] has become an increasing area of research as FFF has grown in popularity. More specifically, mechanical properties of forced deposition

printed materials for robotics applications both in general [8,9] and for nuclear environments [10,11] has become an active area of study.

Applications for 3D printed components in radiation environments include use aboard spacecraft [1,3]; in robots and remotely operated vehicles (ROVs) for nuclear power stations, fuel reprocessing plants [12] and nuclear incidents [13]; unique jigs and tooling for hot-cell systems and medical devices exposed to radiation sterilization [14]. These environments deliver a range of dose rates of gamma radiation. The space adjacent to spent fuel assemblies is typically exposed to 2 MGy in a year of operations [15,16]. Preliminary investigations into the Fukushima Daiichi incident revealed dose rates [17] such that ROVs designed for exploration of the surrounding area must be capable of operating after receiving dose of the order 10–100 kGy [13] in a few days. Highly active radiation conditions can be encountered even within laboratory settings. For example, the equipment for storage of activated samples in the University of Manchester's Dalton Cumbrian

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Facility is expected to receive doses of 2 MGy over the first 1000 h of storage, and materials within 10 cm of the beam target are expected to receive ~ 6 MGy/year of continuous operations. Finally, widely practised sterilization of medical devices relies on a standard dose of at least 25 kGy [18]. For specific applications, researchers have developed specialist filaments for neutron shielding made from ABS/B₄C mixtures [19] and for X-ray shielding made from PC/W mixtures [20]. Such a wide gamut of important practical applications justifies the need for investigation into the radiation hardness of 3D printed structural components to establish the dose range for their reliable functional performance.

The existing literature on FFF concludes that a wide array of parameters, including infill pattern orientation [5], print temperature [21], fibre colour [7] and post-printing heat treatment [22], have a direct effect on the layer adhesion and various mechanical properties. Other work has identified gamma dose levels, irradiation temperatures and additives to be used in manufacturing to promote cross linking without resulting in excess chain scission with the intent of improving interlayer adhesion and reducing mechanical anisotropies [23]. The 3D printed plastics have specific pore structures modified by printing parameters [24] which affect the efficiency of oxygen diffusion into the bulk of the material. It is known that O₂ diffusion plays an important role in radiation-induced reactions in polymers [25,26]; hence the oxygen present in porous FFFs might alter the reactions of radicals produced by the irradiation of 3D printed polymers significantly in comparison to the conventional (less porous) synthetic materials. It is evident that infill pattern and print density drives porosity [27] and oxygen diffusion. Oxygen diffusion strongly affects the reaction pathways taken by the free radicals produced by radiation, and the radiation chemistry drives embrittlement. Embrittlement will affect part ageing and structural damage, which will in turn alter the available diffusion pathways. It would therefore be challenging to extrapolate bulk physical properties of irradiated FFF components from the bulk properties of FFF components and the radiation degradation of irradiated solid parts.

In this article we show that changes in mechanical properties as a result of irradiation are correlated with the structural changes in the studied polymers. The chemical structures of these polymers are shown in the [linked research material](#). We believe that the work presented here is useful for roboticists and other engineers who may be considering the use of FFF-formed materials in high-radiation environments. This work will also provide important information about the extent of radiation effects on bulk properties of FFF materials.

2. Experimental

2.1. Printing

Printing filaments were obtained from 3DGBIRE Ltd. As common for commercially-available polymers, the precise composition of supplied fibres couldn't be found. A pair of desktop grade material extrusion 3D printers (Utilimaker 2 and 2+) was used to print dogbone-shaped samples (Fig. 1, left). The gauge thickness of 1.4 mm was chosen to represent the typical wall thickness of 3D printed structural components produced by off-the shelf FFF printers.

Dogbone samples were printed with the parameters set out in Table 1. These correspond to the manufacturer's guidance, except where this made printing impossible. Altered values are asterisked. The majority of samples used in this work had 0.8 mm thick walls that followed the outline of the samples surrounding an infill pattern at the angle shown in Fig. 1; samples for Polycarbonate were printed with 2 mm thick walls. Several other samples received 2 mm thick walls; these have been excluded from calculations of mechanical properties except where they were the only available specimens for that material and dose level (i.e. PLA 100 kGy, CPE + 1.905 MGy). Table 2 identifies which wall thickness was used for each sample.

2.2. Tensile testing

The samples' tensile properties were measured using the hand operated test-rig shown in Fig. 1, right. The specimen was held by 4 mm diameter rods through the eye holes shown in the sample diagram in Fig. 1. The nut was tightened at a constant rate to apply the strain rates given in Table 3. Force values were recorded by hand. For tensile testing the average stress in the specimen, at any given load, was determined by dividing the force by the cross-sectional area.

High-resolution images (1 pixel = 0.01 × 0.01 mm) of the sample under strain were recorded at fixed intervals, and strain maps were prepared using the DaVis digital image correlation (DIC) software [28]. The correlation mode was "sum of differential", the subnet size was 75 × 75 and a maximum expected deformation of 512 pixels was used. No additional speckle pattern was applied; in most cases, the natural surface variation from printing was sufficient, although PC samples, which had better surface finish, posed challenges to the analysis. Linear strains were extracted for use in calculation of Young's Modulus (YM). DIC is unaffected by strain outside of the area studied, so stretching around the attachment positions was discarded.

For the unirradiated Nylon and the TPU, alterations were made to the test rig to allow for strains of up to 700% to be measured. In these cases, strain was measured as a function of screw position rather than being limited by the narrow field-of-view of the camera. This experimental set up provided typical instantaneous errors of ± 1 MPa stress and $\pm 0.1\%$ strain, however systematic errors from uneven strain rates are harder to quantify. In addition, the reliability of the image correlation was strongly affected by lighting and sample surface finish. Strain rates and sampling rates were varied depending on the flexibility of the sample as given in Table 3. All tests were performed at room temperature.

The number of successful repetitions for each material and radiation dose is given in Table 2. For all cases, 10 specimens were attempted at 0 Gy, 5 for doses in the 0.1–2.6 MGy range and 8 for doses in the 3.6–5.2 MGy range. An attempt at measurement of YM and ultimate tensile strength (UTS) was considered successful if they failed on the narrow portion of the specimen and the DIC was capable of tracking extension.

Universal test machine tensile testing was performed on unirradiated specimens using an Instron 1122 UTM, using a load cell of 0.5 kN and a grip distance of 35 mm to provide a baseline for variation between samples. The number of samples is as listed in Table 2. All tests were performed at room temperature.

2.3. Sample irradiation

Irradiation was performed in a Foss Therapy self-shielded ⁶⁰Co irradiator. Samples were exposed to gamma ray doses in the range 0–5.3 MGy as stated in Table 2. Dose rates of 13.3 ± 0.9 kGy/h were used for all samples, except for the PLA, which were placed further from the source to obtain lower total doses and prevent sample heating; these received dose rates of 6.2 ± 0.1 kGy/h. Dose rates were determined by using a Radcal® in equivalent positions within the irradiator. The air temperature in the irradiator rises to around 45 °C over the course of the first hour of each irradiation period, as the ⁶⁰Co is self-heating. Samples were allowed to rest between the end of irradiation and mechanical testing for 1–4 days, with the waiting time being largely determined by the experimental pipeline.

2.4. Chemical analysis techniques

Gel permeation chromatography (GPC) was used to identify molecular mass and molecular weight of the soluble fractions of the samples before and after irradiation. PLA, PC, CPE and unirradiated TPU were dissolved in THF (Tetrahydrofuran) at 35 °C and analysed using a Malvern Omnisec GPC with a 1 ml/min flow rate. CPE + was dissolved

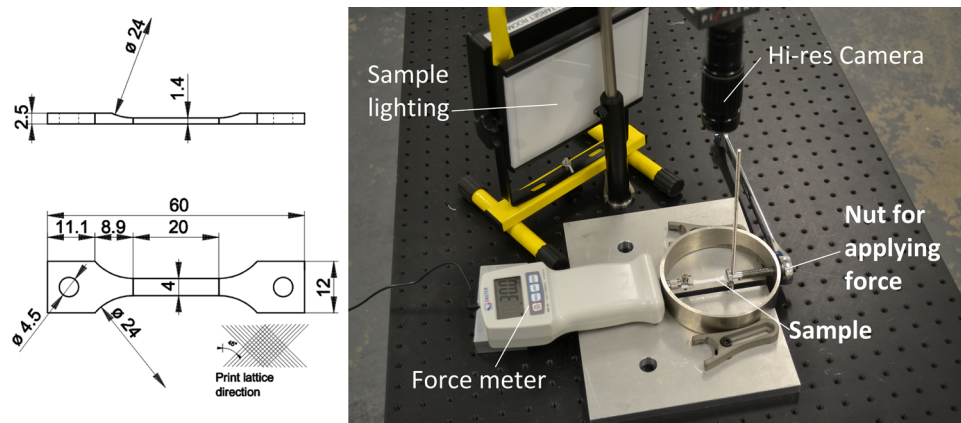


Fig. 1. (left) the physical dimensions (in mm) of the tensile test specimens used in this work (right) the strain rig used in this work.

in Chlorobenzene at 70 °C and analysed with a Gilson 307 pump and an ERC7515A differential refractometer. In both cases molecules were separated using 2 PL mixed B and one 50W0 Å column. The results given are M_n , the number average molecular weight (i.e. there are the same number of molecules heavier than M_n as there are lighter than M_n), and M_w the weight average molecular weight (i.e. there is the same mass of molecules heavier than M_w as there are lighter than M_w).

FTIR and Raman spectroscopy were applied to identify changes to the chemical bonds present in samples. Spectroscopy was performed using a Bruker Vertex 70. FTIR used the Bruker Platinum ATR accessory, and Raman used Bruker RAM II accessory and 1064 nm laser. All spectra recorded at a resolution of 4 cm^{-1} .

In addition, TGA and DSC were used to support the results collected by GPC and spectroscopy for specific polymers. Thermogravimetric analysis (TGA) of chipped polymer samples was carried out using a Mettler-Toledo TGA/DSC 1 device. The analysis were run under nitrogen flux (30 mL/min) at 10 °C/min heating rate from room temperature to 1000 °C. 5–10 mg of each material was used for the analysis. Differential Scanning Calorimetry (DSC) analysis of crushed polymer samples was performed using the Jade instrument from PerkinElmer. PLA specimen were interrogated in the 40–200 °C range whereas Nylon was analysed between 50–300 °C; the ramp rate was 5 °C/min in both cases. The analysed quantity of material was between 5 to 10 mg per run.

3. Results

In the following subsections we describe the tensile testing results at different dose levels, along with results from GPC, FTIR, Raman and thermal analysis which are used to understand the radiation-driven changes to chemical structure, and how these changes drive changes to mechanical properties. We also offer qualitative results of the anisotropies within FFF tensile specimens.

Table 1

The printing parameters used. Unmarked numerals: manufacture's guidance, asterisked: altered values necessary to produce consistent samples.

3D Printing Material Morphology	Materials						
	PLA	ABS	TPU	PC	Nylon	CPE	CPE +
Filament thickness (mm)	3	3	3	3	3	3	3
Material colour	White	White	White	White	Clear / Natural	Clear / Natural	Clear / Natural
Printer make/model				Ultimaker 2+ / 2+ extended			
Nozzle diameter (mm)	0.4	0.4	0.6*	0.4	0.4	0.4	0.4
Extruder temperature (°C)	210	250	235	260	250	250	260
Build plate temperature (°C)	60	80	70	100*	60	70	100*
Layer height (mm)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Infill density (%)	100	100	100	80*	100	100	100
Fan speed (Hz)	100	20	35	0	35	80	25

3.1. Strain map variation following print pattern variation

DIC is a valuable technique for investigating FFF-manufactured components as it captures strain maps which include detailed information of local anisotropies not recorded by universal test machines. This allows observation of local features in the strain field caused by alterations to the print pattern [29]. This is important as it is well known that FFF components can have extreme anisotropies in their physical characteristics determined by print patterns [30,31].

To illustrate how variation in print pattern affects the strain distribution within samples under test, Polycarbonate samples were prepared with different wall thicknesses. Print pattern may be changed by alterations to the slicer parameters or by manually editing the gcode. In this case wall thickness was changed, altering the number of longitudinal print tracks. Other possibilities such as temperature and feed rate will also affect porosity and linking between print tracks. Fig. 2 shows the visual image (top) and a strain map (lower) for samples with 2, 0.8 and 0 mm thick outer walls (left, centre, right). The 2 mm thick wall had $\sim \times 2$ the UTS of the samples without walls at 0 dose.

Fig. 2 (lower, left) has a large glitch in the bottom left; this is typical for thick-walled samples, as the smooth surface finish was difficult for the DIC software to track accurately. Fig. 2 (lower, centre) shows a concentration of stress in the walls. Fig. 2 (lower, right) shows the same information for a sample printed without walls, demonstrating a more even distribution of stress.

3.2. Stress-strain plots

Stress-strain plots were produced from the force data and strain maps using the “strain gauge” routines in the DIC software. Tensile test values such as Y_M (Stress/strain in the proportional region), elastic limit and UTS (the highest stress applied) were determined using these plots. The stress-strain plots for all PC samples are shown in Fig. 3. As

Table 2

The dose levels to which different test specimens were exposed. “No. specimens” is the number of successful repeats used for YM and UTS estimates. Figures in brackets represent thick walled specimens. See section 2.1.

Polymer	Dose and no. used specimens	UTM (Instron 1122)	Digital image correlation					
PLA	Dose (MGy)	0	0	0.097	0.199	0.307	0.338	
	No. specimens	10	9	(5)	2	2	0	
ABS	Dose (MGy)	0	0	0.526	1.341	1.956	2.628	
	No. specimens	9	5	4	2	1	3	
Nylon	Dose (MGy)	0	0	0.666	1.229	1.905	2.623	3.659
	No. specimens	10	5	5	5	5	5	8
TPU	Dose (MGy)	0	0	0.526	1.341	1.956	2.628	5.276
	No. specimens	10	5	5	5	5	5	7
Poly Carb	Dose (MGy)	0	0	0.666	1.229	1.905	2.623	
	No. specimens	10	(4)	(3)	(5)	(5)	(5)	
CPE	Dose (MGy)	0	0	0.624	1.215	1.903	2.551	
	No. specimens	5	5	5	5	4	5	
CPE +	Dose (MGy)	0	0	0.624	1.215	1.903	2.551	
	No. specimens	9	5	5	4	(2)	0	

Table 3

Approximate strain and data sampling rates of materials in this work.

Material	PLA	ABS	CPE	CPE +	PC	Nylon			TPU
Dose (MGy)	All	All	All	All	Other	0.75	0	0.75	Other
Strain rate (m/s)			$\sim 3.5 \times 10^{-6}$					$\sim 3.2 \times 10^{-4}$	
Sampling rate (Hz)			1/15		1/30		1 × 1/5	1/30	1/15
							4 × 1/25		1/25

stated in section (2.1), specimens were printed with two different wall thicknesses. In the Figure, thick walls are represented by the hollow symbols. UTM and DIC results are plotted next to each other for ease of comparison. See the [linked research material](#) for complete results.

Some samples, notably the unirradiated CPE +, displayed a necking behaviour. This is seen in the CPE + stress-strain plot as a plateau after the elastic yield point. TPU and unirradiated Nylon samples showed deformation around the eye holes. Figs. 4 and 5 show the mean values for mechanical properties extracted from the samples of each dose level and material. Hollow symbols represent those cases where only thick-walled specimens were available; in other cases, values for thick walled samples were discarded. The DIC tensile rig had too slow a sampling rate to give stress-strain values from unirradiated Nylon or TPU before reaching the elastic limit; the YM values from the DIC strain rig are therefore a minimum limit, which is consistent with the data from the universal test machine (UTM).

The evolution of the ultimate tensile strain (UTS) and elastic limit for each material with increasing dose is shown in Fig. 4. Elastic limit is only available for Nylon at 0 dose using data from the UTM. Stress-strain data extracted using the DIC strain rig did not have the resolution to identify the elastic behaviour. The figure shows that UTS decreases with dose except in the case of Nylon.

The UTS of the materials followed several distinct trends with increasing dose. PLA degrades extremely quickly, with UTS dropping to half of the original value at 0.2 MGy. The observed values are within errors of those seen in Ref. [2], despite differing strain rates. Low radiation tolerance is a known feature of polymers with methyl groups [32]. CPE, CPE +, ABS and TPU undergo near monotonic decreases in UTS reaching minimum values and plateauing at 1.9, 0.6, 1.3 and 1.9 MGy respectively. PC displays near-monotonic decrease of UTS with increasing dose up to the maximum recorded value of 2.6 MGy. In sharp contrast to other materials, the UTS of Nylon is more or less constant up

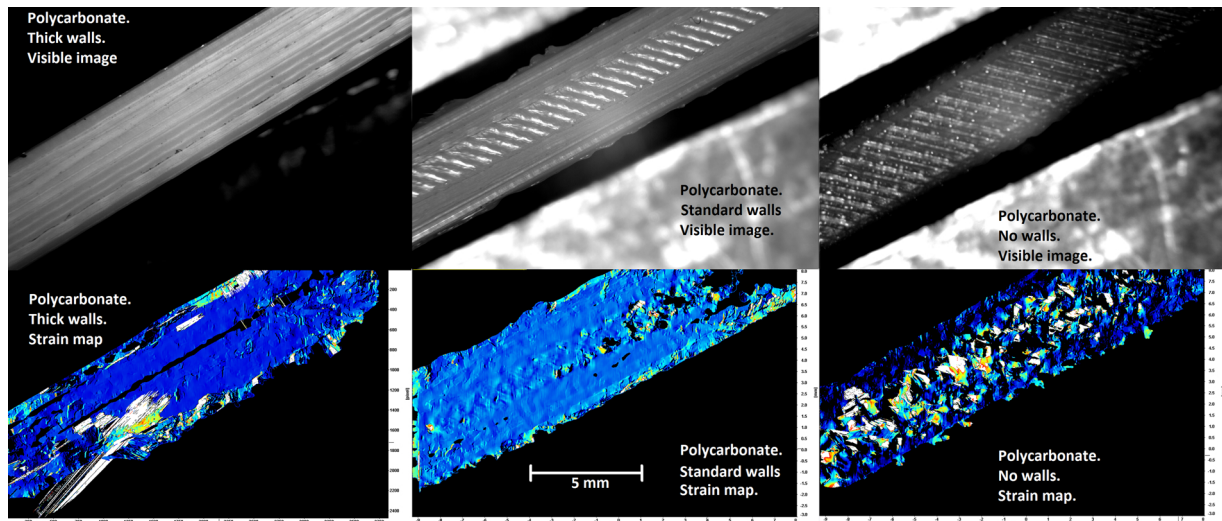


Fig. 2. Visual and DIC strain map images of PC samples printed with different wall thickness.

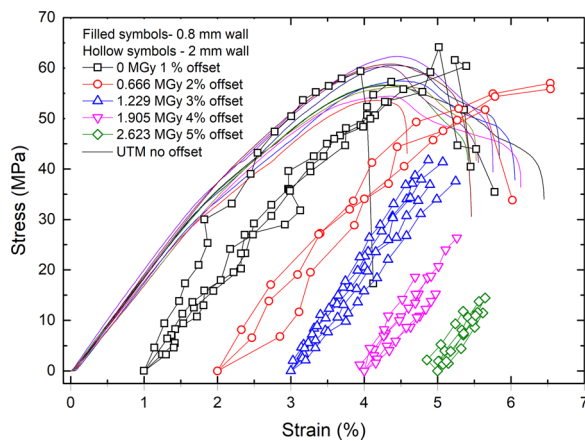


Fig. 3. Stress-strain plots for PC. For clarity, values from the DIC tensile rig are offset depending on received dose. Lines link points from the same specimen. Multiple lines indicate repeats to ensure reliability. Bare lines from UTM tests.

to the maximum received dose of 5.3 MGy. The slight increase observed between 2.6 and 3.6 MGy coincides with a change between print batches, but since the batch exposed to higher dose was on average 4% lighter it seems unlikely that the changing print conditions made the samples stronger.

The evolution of YM with increasing dose is shown in Fig. 5. The figure shows essentially unchanging values for CPE, CPE+, PC and TPU. PLA values reported here are within errors of each other up to 200 kGy, and are also within errors of values from Ref. [2], although the smaller reported errors in that work allow a gradual stiffening trend to be observed up to the maximum observed dose of 150 kGy. The larger dose range in our work also shows a rapid decline in YM of PLA at the end of its radiation tolerance between 200–300 kGy. The YM of ABS, both in this work and the literature [1] shows a slight increase across the entire range of applied doses (0–2.6 MGy). CPE+ shows a similar behaviour, with a slight increase up to 1.2 MGy, and then a rapid decline in the range 1.2–1.9 MGy, although this final value is from a single sample with a different print pattern, and may represent an

independent trend. The YM of Nylon shows steady increase from 0 to 1.229 MGy, the value then remains constant up to the maximum received dose of 5.276 MGy. The strain at yield decreased from $250 \pm 25\%$ to $12 \pm 3\%$; this change may impose limitations on the usefulness of Nylon as a structural material.

For both UTS and YM, comparison between results from DIC and the UTM show that they are within errors of each other. The YM of samples tested by UTM had an average standard deviation of 70 MPa, compared to 210 MPa for samples measured using the DIC rig; this shows that there is some variation between specimens due to variability in the production process, but that the majority of the reported variation is from inconsistencies in the strain rate applied by the hand-operated rig. We may therefore be confident that the applied strain rate was similar to that obtained using automated test machines. The measured YM and UTS of irradiated 3D printed ABS and PLA also shows good agreement with literature values [1,2].

3.3. GPC results

The mass of the polymer molecules as measured by GPC is indicative of the predominant radiochemical processes affecting the materials, either the formation of cross-links and an increase in average molecular mass, or main chain scission and a decrease in average molecular mass. These chemical changes drive the changes to mechanical properties seen in the measures of the UTS and YM. GPC analysis of the Nylon and ABS was not possible, as they would not dissolve in the available solvents and the temperatures possible with the equipment. GPC analysis is not available for TPU post-irradiation as it had become insoluble. This is indicative of extensive cross-linking and an increase in molecular mass. PLA underwent the largest reduction in molecular mass, even though it was exposed to much lower radiation doses; this rapid and extensive break-up of the molecules is indicative of an extreme radiation sensitivity and vulnerability to main chain scission. GPC of CPE+ shows a bimodal distribution, presumably of CPE and an additive referred to as “+” by the manufacturer. GPC analysis of post-irradiation CPE+ is only available for the lower-mass peak, as the high-mass peak is completely removed, indicating high levels of chain scission for this set of molecules. The lower mass peak of CPE+ underwent

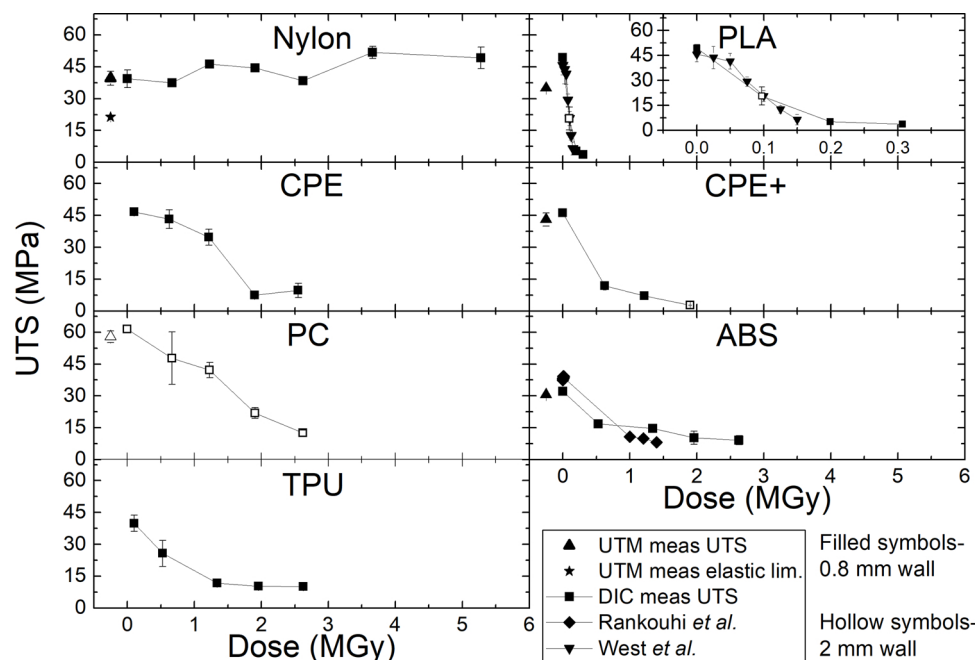


Fig. 4. UTS and elastic limit (where available) of tested materials as a function of received dose. Lines are to guide the eye. UTM values at 0 dose have been offset to aid clarity. Error bars represent the statistical scatter of the multiple specimens. Values from this work, [1], [2], [3].

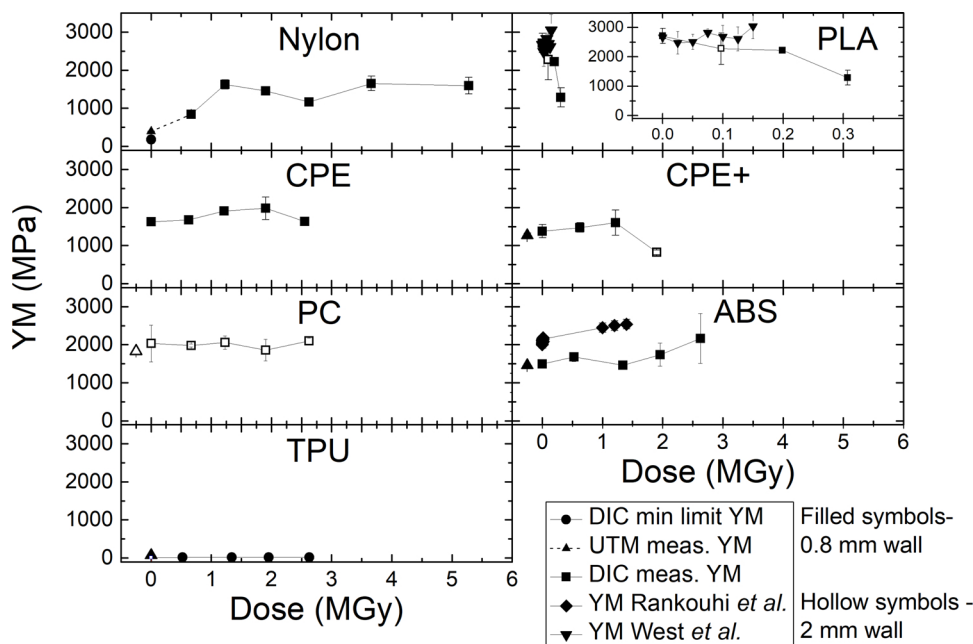


Fig. 5. YM for all tested materials as a function of received dose. Lines are to guide the eye. Dotted line joins UTM measurement with DIC tensile rig measurement. Hollow shapes indicate a lower limit on a value that could not be extracted from the stress-strain curves. UTM values at 0 dose have been offset to aid clarity. Error bars represent the statistical scatter of the multiple specimens. Values from this work, [1–3].

Table 4

GPC results of change to average molecular mass before and after irradiation.

CPE				PLA		
Dose (MGy)	0	2.5	Fraction	0	0.64	Fraction
Mn	2.1×10^4	8.6×10^3	0.41	7.9×10^4	3.4×10^3	0.04
Mw	6.8×10^4	3.7×10^4	0.53	1.5×10^5	1.2×10^4	0.08
PC				CPE+ (lower peak)		
Dose(MGy)	0	2.6	Fraction	2.5	After	Fraction
Mn	2.4×10^4	8.0×10^3	0.34	2.1×10^4	2.0×10^3	0.10
Mw	5.0×10^4	2.4×10^4	0.47	3.7×10^4	9.7×10^3	0.27

more mass loss than the corresponding mass peak in CPE, possibly indicating that the higher mass molecules drive radiation chemistry such as to increase chain scission. Macromolecules of CPE and PC decrease in mass at approximately the same rate. GPC results are given in Table 4.

3.4. Spectroscopy results

Complete FTIR and Raman spectroscopy results including comparison between the FTIR spectra of the most irradiated and unirradiated samples for a given material are given in the [linked research material](#). Peaks are assigned based on Refs. [63,68–83]. Raman spectroscopy, like FTIR spectroscopy, is often insensitive to crosslink formation and main chain scission, because it only requires to the formation or breaking of an individual chemical bond to double or half the mass of the molecule, and this will make a negligible change to the Raman spectrum. Where cross-links are a unique chemical bond they may be visible as a new peak. In this section we compare the vibrational spectroscopy results to highlight radiation-induced change.

Virgin CPE/CPE+ FTIR spectra are very similar. The spectra also undergo similar changes with increasing dose in air. Spectra were normalised on the 722 cm^{-1} peak assigned to C–H and so it is not meaningful to compare the intensity of C–H peaks with increasing dose. The main observed change with dose is the growth of the 1697 cm^{-1} peak. This, like the pre-existing 1714 cm^{-1} peak is assigned to C=O in a plasticiser [33]; the different peak position may reflect changes to the environment around the carboxyl group in the plasticiser or the creation of new carboxyl groups on the CPE (using atmospheric oxygen). In this case the peak growth would correlate to main chain scission. For CPE+, no additional absorption spectra changes occur

that could be assigned to the complete removal of the higher-mass peak. The other peaks do not exhibit noteworthy changes. Raman spectroscopy of CPE and CPE+ shows only minor variation with increasing dose.

PU FTIR spectra were normalised on the 1165 cm^{-1} peak assigned to C–O stretch. The main changes with dose are the disappearance of the peaks associated with the urethane groups, mainly, 509 , 1255 , 1527 , 1700 and 3328 cm^{-1} . In addition, there is also a small decrease in the bands at $2800\text{--}3000 \text{ cm}^{-1}$ due to C–H₂ stretches, a small increase in the N–H stretch due to free amines at 3450 cm^{-1} and, the peak at 1728 cm^{-1} , associated with the ester C=O stretch, remains constant. This suggests that there is C–H bond cleavage, as well as cleavage of the amide bond (i.e. main chain scission and molecular mass reduction) causing an increase in the free amide band. Interestingly, the 1097 cm^{-1} peak assigned to C–C–C backbone vibration does not increase with dose. Raman spectroscopy of TPU shows growth of a minor peak at 1155 cm^{-1} , attributed to a C–O–CN symmetric stretch due to cross-linking. This reaches a maximum after 1.341 MGy , but otherwise shows only a slight increase in background with increasing radiation dose.

PC FTIR spectra were normalised on the 1188 cm^{-1} peak assigned to C–O stretch. In general, changes to the spectra with radiation dose were small and this radiation stability is expected due to the large number of aromatic groups in the PC structure. The main changes with increasing radiation dose are the disappearance of the peaks associated with the C=O groups at 1727 and 1769 cm^{-1} , as well as a small decrease in the aromatic C=C stretch at 1503 cm^{-1} and the appearance of a very broad band centred around 3200 cm^{-1} attributed to hydroxyl groups. In addition, we also observe a small increase in the carbon dioxide peaks around 2300 cm^{-1} . This suggests that there is initially

chain scission at the C–O ester linkage to form both a carbon-centred and an oxygen-centred radical. Indeed, this is the radiation-induced mechanism proposed by Sinha et al. [34], and is also one mechanism of the UV ageing of PC suggested by Tjandaatmadja et al. [35]. Decarboxylation can then occur from the carbon-centred radical, resulting in an increase in the carbon dioxide signal (as observed), followed by a photo-fries rearrangement to produce hydroxyphenyl or hydroxydiphenyl compounds, consistent with the broad IR signals observed at around 3200 cm^{-1} . Raman spectroscopy of PC shows only minor variation with increasing dose.

PLA FTIR spectra were normalised on the 1082 cm^{-1} band associated with one of the CO stretching modes. A comparison between FTIR spectra of unirradiated PLA with the samples exposed to gamma radiation revealed the growth of all main characteristic bands, i.e. the –C–C–, –C–O– and –CH– peaks, upon irradiation. The peak at 1731 cm^{-1} , associated with the carbonyl group C=O, grows with increasing radiation dose; this peak growth is also shown in [2]. However, the second carbonyl related band at 1750 cm^{-1} is not affected by irradiation. Raman spectroscopy of PLA shows the addition of peaks at 540 cm^{-1} , assigned to C–CH₃ deformation that appears as the polymer becomes more crystalline [38] and 2860 cm^{-1} assigned to a C–H stretch; this may be caused by an increase in the number of polymer chain terminators following chain scission [39]. Other peaks appear at 2030 , 2085 and 2230 cm^{-1} , assignment to which is more difficult, although at least one could be due to a C triple bond C stretch. The size of these peaks does not change appreciably past 0.624 MGy .

ABS FTIR spectra were normalised on the 698 cm^{-1} band. Administering radiation to this polymer produces only minor changes in the IR spectra. The functionalities which appear to be most affected by radiation are the 1,2 and 1,4 butadiene C–H units; the associated bands become gradually reduced with increasing dose. In parallel, broad structure between 1600 – 1800 cm^{-1} becomes more pronounced upon irradiation, suggesting the formation of additional carbonyl groups. Hence, butadiene fraction in the ABS polymer seems to be a primary target for radiation induced degradation. These observations are in accord with the published literature [36]. Raman spectroscopy of ABS shows an increasing background/reduced peak height with increasing dose. This may be indicative that the chemical structure is becoming more random.

Nylon FTIR spectra were normalised on the largest (1633 cm^{-1}) peak associated with C=O stretching. It has been found that irradiation affects all major peaks at 3300 cm^{-1} , 2930 and 2860 cm^{-1} , 1633 and 1690 cm^{-1} , as well as 1250 cm^{-1} ; the effect is indicative of significant chemical changes in this system. The most remarkable changes concern an increase of free amines (1250 cm^{-1}) and carbonyl groups (1690 cm^{-1}). The observed trend agrees well with the literature [37]. Formation of these degradation products is symptomatic of the chain scission process. The growing broad feature seen between 3400 – 3600 cm^{-1} , is assigned to reactions with water vapour in the air producing hydroxyl groups. Raman spectroscopy of Nylon shows only minor variation with increasing dose.

3.5. Additional observations

3.5.1. PLA

In an initial series of irradiations, PLA received the same dose rates as the other samples. The high-dose rate PLA samples displayed swelling and the samples broke after swelling caused them to press against the support frame used to hold the samples during irradiation. A “foam” structure was observed in the broken parts, shown in Fig. 6 (top left). PLA samples also displayed weight loss, indicating the formation of volatile organic compounds, which is further indication of chain scission.

The predominance of chain scission process in irradiated PLA was further confirmed by thermogravimetric analysis (TGA) of selected PLA samples, shown in Fig. 7 (top, left). The data indicate that there is a

clear shift towards a lower starting temperature for thermal degradation, which correlates well with the absorbed dose; this is seen in the broad trend indicated by the arrow, and in an enhancement of mass loss with dose in the 80 – 270 °C range, from 0.4% (0 Gy) to 1% (300 kGy). This phenomenon could be due to the dose dependent accumulation of peroxy groups in PLA irradiated in the presence of air; these functionalities are thermally labile and will decompose readily upon heating [41]. It is known that chain scission combined with the loss of –CO–O– groups in PLA will result in the formation of new saturated and unsaturated aliphatic chain-ends [42]. In the presence of air, formed alkyl radicals react with oxygen to give peroxy radicals [41,43]. Thermally induced decay of peroxy radicals in PLA might favour further decarboxylation of the polymer releasing CO₂ as a product.

DSC analysis of the studied PLA samples shows that both the glass transition temperature and melting temperature of the polymer decrease with increasing absorbed dose, suggesting that both amorphous and crystalline phases of PLA change significantly upon gamma irradiation, as shown in Fig. 7 (top, right) [44]. These trends are in line with those reported in [2], although they are offset by 10 and 20 degrees respectively. This may be due to a different mix of additives in the filament.

Lower glass transition and melting temperature in irradiated PLA samples can be explained by: (1) reduction of the average size of both amorphous and crystalline phases in PLA due to radiolytic degradation; (2) accumulation of the volatile, low molecular weight products in irradiated samples. The DSC results provide another piece of evidence that the degradative chain scission processes dominate the radiation chemistry of PLA. It should also be noted that the glass transition temperature at higher doses reduces towards the internal temperature of the irradiator (45 °C); we may therefore expect high-dose PLA to be below its glass transition temperature while under irradiation

3.5.2. Nylon

The Nylon samples become sticky at dose levels of 3.659 MGy or higher; this may render Nylon unusable as a material for moving mechanical parts. Other irradiated Nylons do not display this behaviour.

TGA data shown in Fig. 7 (middle, left) shows evidence in support of the radiolytic formation of low molecular weight products. TGA scans of the Nylon specimen clearly show that the onset of thermal degradation shifts consistently to lower temperatures as the samples receive an increasing absorbed dose. DSC analysis demonstrates changes in the melting point of Nylon samples as a function of absorbed dose. As can be seen in Fig. 7 (middle, right), the initial melting point at 190 °C decreases by about 30 degrees after 3.65 MGy irradiation dose. The trend can be explained by the accumulation of low molecular weight products in the structure of the irradiated polymer, or, alternatively, it can be caused by crosslinking and branching occurring predominantly on the amorphous domains in semicrystalline polymer like Nylon [37]. This crosslinking hinders the formation of crystals on cooling, causing a delay on the crystallisation [40].

3.5.3. ABS

Irradiating ABS to high doses results in the formation of some low molecular weight fragments which are easily volatilised upon heating. Fig. 7 (lower, left) shows the TGA scan of pristine and irradiated (2.68 MGy) ABS. Thermal degradation of irradiated ABS shifts to lower temperatures indicating the presence of volatile low molecular weight products. The production of volatile molecular species, when combined with the spectroscopy data, is further evidence that some radiation-driven chemical changes have taken place.

3.5.4. Colour change

Radiation damage leads to the production of discoloration in some polymer systems. This can be used for opportunistic dosimetry [32] to determine when printed objects need replacing. This colour change may be altered by chemical action or UV radiation. Photos of the

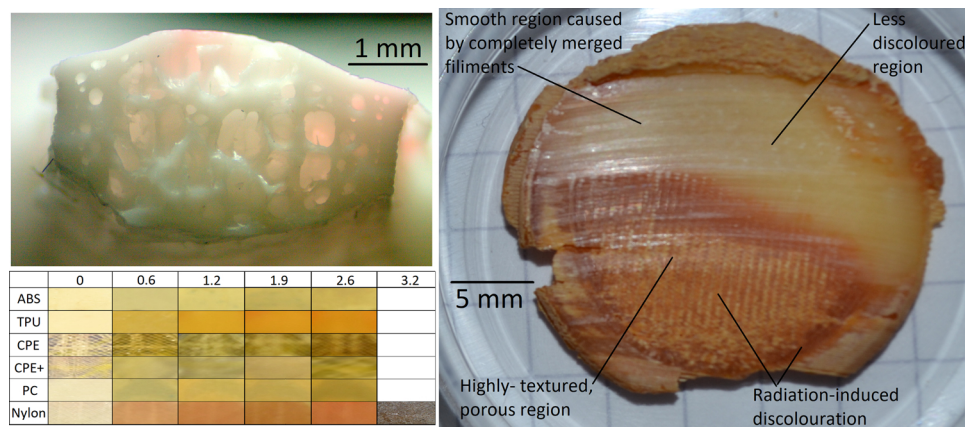


Fig. 6. Photos of irradiated 3D printed samples to show (top left) the broken gauge section of a PLA sample at 0.604 MGy, showing bulk swelling, deformation and “foaming” of the interior; (lower left) colour change of the different plastics during irradiation; approximate total dose in MGy given in the top row (PLA showed no noticeable discoloration up to 400 kGy as is not shown) (right) uneven radiation induced discoloration in a slice from a 3D printed High-impact polystyrene (HIPS) cylinder. The discoloration corresponds to variations in the texture caused by differing print densities. Total dose: 7.068 MGy.

discoloured plastics are shown in Fig. 6 (bottom left). We additionally report on a 3D printed high-impact Polystyrene (HIPS) cylinder approx. 20 mm dia x 50 mm length irradiated to 7.068 MGy. Variations in the printing process lead to changes in the density of the material laid down. A slice cut from this cylinder is shown in Fig. 6 (right). From this it is clear that regions with higher porosity corresponded with radiation-induced discoloration, while relatively dense regions showed less colour change. This supports the idea that radiation-induced chemical changes are strongly influenced by oxygen diffusion and consequently, porosity and print pattern.

4. Discussion

Radiation effects on polymer systems is a well-established field [45], with research on mechanical properties of polymers following gamma irradiation [46,47] remaining an area of great interest. Existing studies on bulk and powdered polymers can be used to place limits on how print pattern and density may affect the radiation chemistry. Irradiation of organic polymers induces the production of radical species that drive chemical reactions thus leading to changes in physical properties that continue even after the sample has been removed from the radiation field. Table 5 reviews literature of the lifetimes of

radiation-produced radical species in various atmospheres vs. vacuum, as determined by electron spin resonance studies. “In air” lifetimes in powders and bulk plastic is likely to differ from that observed in 3D printed materials, as radical recombination can be spatially influenced by diffusion-limited oxidation (DLO) over a length scale of ~ 1 mm over a period of minutes to days [48,49]. The materials tested have similar bulk oxygen diffusion properties [50,51]. FFF-formed materials therefore occupy a middle ground when no part of a print path is > 0.2 mm from an air gap; airflow within the bulk material is dependent on porosity variation within the microstructure. In a part with low infill density, filament orientation will not affect the radiation-induced chemical processes that lead to changes in UTS and YM on the scale of individual filaments. Providing that the structure is sufficiently dense, infill pattern will affect transport of oxygen, so the polymer will experience different radiation-induced physical changes, on top of the differing initial mechanical characteristics. However, detailed analysis of the reaction pathways and mechanisms linking them to environmental factors are beyond the scope of this work. This data shows that allowing the samples to rest for 1–4 days between irradiation and analysis will allow any reactions to complete so that the results reported here correspond only to the final species formed.

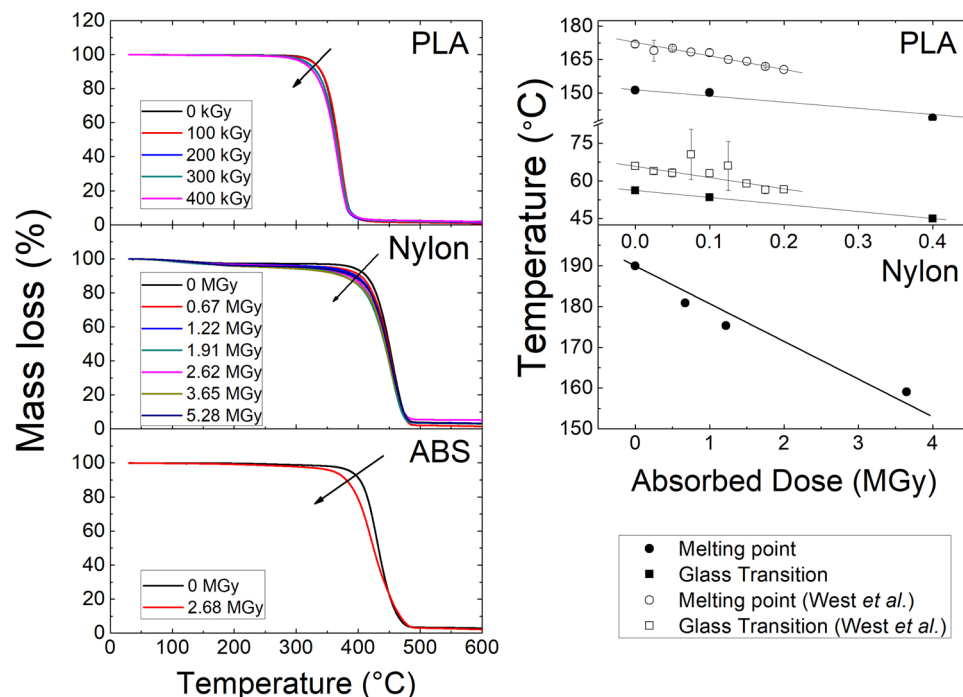


Fig. 7. TGA curves (left) and DSC analysis results (right) for (top) Nylon, (middle row) PLA and (lower) ABS, at various dose levels.

Table 5

Reported lifetimes of radiation induced radicals in relevant polymers. The fraction of radicals assigned to each species at the start of the aging process is given in column 4.

Polymers and irradiation environment	Atmosphere during Irradiation / ageing	Physical description	Lifetimes of radical species
Nylon-6 [52,53]	Vac/vac	filament bundles	species A 70% (fast component) $t_{1/2} = 1.8$ d species B 30% (slow component) $t_{1/2} = 30$ d
Nylon-6 [53]	Vac/air	filament bundles	All species $t_{1/2} = 1.7$ h-4.5 h (dose dependant)
PLA [54]	Vac/vac	Fine powder	All species decay to 30% in 15 min at 300 K
PVC (similar to CPE) [55]	Vac/vac	Powder and 0.010" films (identical results)	species A (83%), $t_{1/2} = 2$ min; species B, $t_{1/2} = 1.9$ d; species C, $t_{1/2} = 19$ d; species D (7%), $t_{1/2} = 1.7$ y 83%
PVC (similar to CPE) [56]	Vac/air	Thin films 20-35 μ m	Polyenyl radicals $t_{1/2} = 8$ min; $\text{CHCl-}\dot{\text{C}}\text{H}-(\text{CH}=\text{CH})_n\text{-CHCl-}$ $t_{1/2} = 5$ h
PC [57]	Vac/vac	0.5 mm film	All species: 25% in 4 min 300 K
TPU [49]	Vac/air and Vac/N ₂	1.5 mm film.	Only species is the peroxy radical: $t_{1/2} = 1.7$ h
ABS [58]	Air/air	2mm dia. 3 mm length	All species: $t_{1/2} = 8-9$ d

Table 6

comparison of results from thermal analysis, spectroscopy, Mass analysis and mechanical testing. The change in UTS is given for the initial slope of Fig. 4. CPE+ uses only the first two values, TPU and PLA use the first 3 values, CPE and ABS use the first 4 values and Nylon and PC use all the points. The change in YM with dose is given for the slope in Fig. 5. CPE+ uses the first 3 values, CPE uses the first 4 values, ABS, PLA and PC use all available values. ABS and Nylon have separate slopes calculated for points 1–3 and 3–5 and 3–7 respectively. All slopes have error-weighted fits. Mechanical testing cells are highlighted green to indicate increasing characteristics, red to indicate decreasing characteristics and grey for no/minor changes. CS indicates that analysis of data from a technique was indicative of chain scission; CL indicates that analysis of data from a technique was indicative of crosslinking.

Polymer	TGA	DSC	UTS	YM	GPC results			Spectroscopy		Dominant mode
			dMPa/MGy	dMPa/MGy	dMn (%)	Dose	CL/CS	Raman	FTIR	CL/CS
CPE	No data	No data	-20.5 $\pm$ 0.4	150 $\pm$ 60	41	2.5	CS	Inconclusive	CS or mod. additives	CS
CPE+	No data	No data	-55 $\pm$ 4	170 $\pm$ 23	10	2.5	CS	Inconclusive	CS or mod. additives	CS
ABS	CL	No data	-11.4 $\pm$ 0.7	80 $\pm$ 160; 500 $\pm$ 400	NA - insoluble			Inconclusive	CL up to 0.5 MGy; CS	CL
ABS (Lit) [1]	-		-23 $\pm$ 2	350 $\pm$ 70	-					
PLA	CS	CS	-220 $\pm$ 10	-4000 $\pm$ 1000	4	0.64	CS	CS	CS	CS
PLA (Lit) [2]	-		-290 $\pm$ 22	1770	-					
Nylon	CS	CL or small fragments	2 $\pm$ 1	1100 $\pm$ 75; -30 $\pm$ 50	NA - insoluble			Inconclusive	CS	CL
PC	No data	No data	-18.6 $\pm$ 0.8	60 $\pm$ 40	34	2.6	CS	Inconclusive	CS	CS
TPU	No data	No data	-21 $\pm$ 3	>20	Became insoluble, CL			CL	CS	CL

4.1. Comparison of mechanical and chemical changes

Table 6 shows comparison between the change with radiation dose of the mechanical properties of the polymers, the changes in their molecular mass and the conclusions about radiation driven chemical processes that we drew based on spectroscopy and thermal analysis. From this table it becomes clear that the well-known effect of crosslinking resulting in increasing stiffness is in effect [62]: Nylon and TPU show evidence of crosslink formation, and ABS is expected to cross-link from its behaviour under UV; ABS and Nylon show evidence of increasing YM and it was not possible to see if TPU has become stiffer as its extreme elasticity put it outside the resolution of the DIC tensile rig. Literature values for PLA show slight stiffening, but we did not produce evidence for crosslinking. CPE, CPE+, PLA and PC all showed indications of radiation-induced chain scission, and a corresponding loss of molecular mass. This is seen to correspond to a loss in UTS, in accordance with the well-known polymer behaviour that strength scales with molecular mass up to a maximum limit [64]. We therefore assign chain scission and the accompanying loss of molecular mass to be the driver for this physical change.

CPE and CPE+ show some evidence of chain scission as the predominant radiation effect. FTIR and Raman spectroscopy show no major change to peaks assigned to CPE or CPE+. In FTIR, there is a strong growth of a peak assigned to carboxyl groups, indicative of either main chain scission, or of ongoing evolution to the C=O bonds present in additives. The GPC results show decrease in the average mass of molecules in the peak present in both spectra and complete removal of the "+" mass-range molecules in CPE+. This implies that chain scission is the dominant radiation chemistry process and that not only is the additive particularly susceptible, but that it enhances the breakdown of CPE. The UTS and YM of CPE degrade in concert with these changes to the chemical structure, with CPE+ showing reduced performance.

ABS predominantly forms crosslinks below the dose level of 0.526 MGy. FTIR data of ABS shows near-complete loss of the butadiene bands at 0.5 MGy. The UV induced degradation of ABS polymer has been shown to lead predominantly to crosslinking [60]; it is therefore reasonable to expect that crosslinking is also prevailing under the gamma irradiation conditions applied here. Crosslinking in ABS is likely to be favoured due to very high yield of crosslinks ($G_{\text{crosslinking}} = 2\text{--}10$ bonds/100 eV, [61]) of the polybutadiene component in the polymer. If

cross linking is ongoing at higher doses is less certain. This cross-linking is thought to drive the increase in YM observed in the mechanical test results, although this seems to be a more gradual trend up to the maximum dose measured. The ongoing growth of FTIR bands associated with carbonyl groups indicates that radiation-driven chemistry continues at all dose levels. This is presumed to include at least some chain scission driving the ongoing reduction in UTS seen in the mechanical test data. The Raman results are inconclusive, although the increase in background with dose may be indicative of an increasingly random structure. No GPC results were available and TGA results indicate production of volatile, low molecular weight products.

PLA predominantly undergoes chain scission processes. This is supported by the observation of the 2860 cm^{-1} Raman peak (assigned to C–H stretch and caused by an increase in the number of polymer chain terminators following chain scission); it is also supported by the decrease in intensity observed for all major bands seen in FTIR, especially the carbonyl group, C=O. GPC shows the largest observed average molecular mass reduction at relatively low dose levels. TGA analysis shows that increasing dose correlates with lower starting temperature for thermal degradation. This is assigned to the production of peroxy groups; this reaction will also cause chain scission and formation of new saturated and unsaturated aliphatic chain-ends [42]. DSC analysis shows that both the glass transition temperature and melting temperature of the polymer decrease with dose, which could be associated with accumulation of the volatile, low molecular weight products in irradiated samples or with reduced phase sizes. At doses up to 200 kGy the YM of PLA is relatively unchanged, in broad agreement to the slight increase seen in Ref. [1]; no evidence for cross linking is seen which could explain this increase. At doses above 200 kGy, a dramatic reduction in YM is seen, which we assign to the decrease in glass transition temperature. PLA's low glass transition temperature is also known to drive its natural aging processes [59], so the radiation-induced decrease will result in faster natural ageing. We theorise that samples irradiated to high dose were both heated and displaying reduced GT, resulting in the sample being in the viscous state during irradiation; the enhanced mobility of specimens under irradiation allowed the residual strain from the printing process to drive the deformation shown in the top left of Fig. 7. We believe that the observed chain scission is responsible for the rapidly decreasing yield point observed in physical test data.

Nylon shows strong evidence for both chain scission and cross-linking with increasing dose. FTIR spectra show growth of bands associated with low-mass by-products of chain scission; TGA analysis also shows evidence in support of the radiolytic formation of low molecular weight products, i.e. as a result of chain scission, while DSC results support either the production of light molecular weight products or crosslinking and branching occurring predominantly on the amorphous domains in semicrystalline Nylon. However, the mechanical tests involving irradiated Nylon unambiguously show the increase in YM with radiation dose up to 1.229 MGy and unchanging yield point; this allows us to conclude that the crosslinking remains a dominant radiation effect. We therefore conclude that both processes are taking place. The Raman results are inconclusive and no GPC results were available. From our additional observations, the increased stickiness is observed above 3.6 MGy, which would render irradiated Nylon unsuitable for mechanical parts, is thought to be a feature of some additive to this particular commercial filament. This suggests the possibility of preparing other Nylon blends as printer filament which could increase the dose range in which 3D printed parts form useful structures, making them more attractive for high-dose environments. It is also conceivable that other commercial-off-the-shelf Nylon print filaments might display more attractive radiation properties.

Nylon displayed evidence of chain scission without a corresponding decline in UTS. This may be due to a known oxygen-diffusion and dose-rate effect; high dose rates lead rapidly to completely depleting the oxygen present in the material, which cannot be resupplied due to

limited diffusion rates. Nylon therefore undergoes the rest of the irradiation in an essentially anaerobic regime (with a skin effect), displaying only a very small decrease in tensile strength. This has been observed for 0.4 mm Nylon-6 monofilaments exposed to 2000 Gy/hour in Ref. [66]. The samples in this work were exposed to lower dose rates but have a larger bulk, which will further limit oxygen diffusion.

PC shows evidence of chain scission as the predominant radiation effect. Although Raman results are inconclusive, the FTIR data show definite, if small, changes to peak structure which are associated with chain scission. The GPC results also show a decrease in the average mass of molecules, supporting this observation. This reduction in mass correlates with a decrease in UTS, as observed in the mechanical test results.

TPU shows considerable evidence of chain scission but also competing crosslinking. This results in a marked change in chemical properties such as solubility while maintaining relevant physical properties. From FTIR data, irradiation of TPU appears to predominantly drive scission; peaks change in a way that is assigned to cleavage of C–H and amide bonds. However, an increased peak in the Raman spectra is consistent with the formation of C–O–CN cross links. Only a small fraction of total bonds undergo these competing processes, resulting in the production of an insoluble macromolecule which maintains extreme elasticity and shows monotonic decrease in UTS radiation dose up to a maximum at 1.9 MGy. This degree of crosslinking is associated with a decline in tensile strength and a reduction in inelastic stretching [65]. Either process could explain the decreasing UTS.

5. Conclusions

Correctly-selected 3D printed plastics are a suitable option for short-run manufacture for use in environments where they will be exposed to gamma rays. A selection of off-the-shelf filaments was tested. Development of blends incorporating high levels of antioxidants such as Tris(2,4-di-tert-butylphenyl)phosphite is a possible avenue for further extending the suitable range.

Print density was identified to affect radiation-induced discolouration, implying that fine control of the printing process can alter radiation chemistry. We believe that the rate of oxygen diffusion within the component is controlled by the porosity, which can be controlled by the printing parameters in ways not available to subtractive manufacture [27]. However, the slicer parameters which most strongly affect this behaviour are not well understood. Ref [67]. shows that cross sectional air gap percentage decreases from 5.26% to 0.3% for layer thicknesses of 0.4 and 0.2 mm; this may strongly affect the radiation chemistry, as there is less free oxygen available within the material. However, the maximum distance between pores, which would affect the diffusion of oxygen through the plastic increases slightly, with average values of 0.39 and 0.44 mm respectively. If the pores connect to atmosphere and are acting as conduits rather than reservoirs, this will still lead to a reduction in the availability of oxygen, but to a much smaller degree. It is possible that infill patterns with high local densities would be more radiation tolerant for the same mass of plastic than the evenly distributed lattices that are commonly used. There may also be enhancement to be gained by modifications to the extruder head and the starting porosity of the filament. How control of these aging effects will interact with anisotropies in material performance caused by infill patterns will require further research.

Nylon was found to retain its UTS up to 5.3 MGy, but it was observed to undergo a considerable increase in YM up to 1.2 MGy, and this may result in a significant change in the overall stiffness of structural components made from this material. The stickiness of this particular commercial blend at doses above 3.6 MGy will render it unattractive for some uses. Additionally, Nylon's radiation tolerance is known to have a strong dose-rate effect, with slower dose rates causing a greater loss of tensile strength.

If the increasing YM of Nylon is unsuitable for an application as a

structural member of a 3D printed item such as a robotic component, PC or CPE could be a suitable alternative as they retain up to 70 or 75% of their UTS at doses up to 1.2 MGy. Radiation-induced discolouration shows potential for use in practical dosimetry of 3D printed components, allowing replacement towards the end of their useful lifetime.

Declaration of Competing Interest

None.

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