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Reviewed Paper

OPTIMISING THERMOPLASTIC POLYURETHANE FOR DESKTOP LASER SINTERING

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Abstract

Laser Sintering (LS) is an industrially relevant Additive Manufacturing method that has become more accessible since the introduction of commercially available desktop-LS systems. However, useable materials are currently limited to several grades of nylon, and so the aim of this study was to optimise an unknown, novel material for use in desktop-LS. A grade of thermoplastic polyurethane (UNEXTPU) was analysed to determine thermal properties, particle characteristics and bulk powder flow efficiency. To facilitate laser absorption at 445nm, a carbon additive (graphite) was added to UNEXTPU; the addition of graphite also significantly improved flow efficiency. UNEXTPU was successfully processed on a desktop-LS system, and mechanical testing found that it possesses properties comparable to industrial grade thermoplastic polyurethanes (Elongation at Break: 139%, Tensile Modulus: 48.7Mpa, Ultimate Tensile Strength: 7.9Mpa, Shore Hardness: 75). Bulk powder flow efficiency and mechanical properties were retained in twice recycled powder. This research has established a new viable elastomeric material for use in desktop-LS.

Keywords: Additive Manufacturing; Laser Sintering; Desktop-Laser Sintering; Thermoplastic Polyurethane; Powder Characterisation; Mechanical Properties

Introduction

Laser Sintering (LS) is an Additive Manufacturing (AM) method that is receiving widespread interest from high-end sectors of industry [1]. In LS, powdered material is deposited across a build area by a roller or blade, and regions are selectively fused by laser energy. Three-dimensional parts are built in a layer-upon-layer fashion, and unfused powder acts as support material that may also be recycled for further use [2]. The recent introduction of several commercially available desktop-LS systems has made LS technology both accessible and affordable, yet like their industrial counterparts, desktop systems are severely limited by the number of useable materials available [3]. This represents a significant research opportunity for material development, as important sectors of industry have recognised the potential of LS technology since it allows for production of low cost parts that are geometrically complex, mechanically sound and require minimal post-processing [4].

Thermoplastic Polyurethane (TPU) elastomers are block-copolymers consisting of both hard and soft segments [5]. The mechanical properties of TPU are defined by the ratio of hard to soft segments; hard diisocyanate segments give TPU useful plastic properties, such as high tensile strength. The soft segments consist of polyether or polyester based diols which connect

the hard segments, and are responsible for elastic properties in TPU. There are several commercially available grades of TPU that are optimised for use in industrial LS systems, but currently none are optimised for desktop systems, and the literature concerning desktop-LS useable TPUs is sparse. The market potential for TPU is high, and thus it has received attention from affluent sectors of industry by way of investment into research & development, particularly in AM [6]. TPUs possess many desirable properties, such as high elasticity and resistance to chemicals and abrasion, making them potentially useful for a variety of applications, such as clothing, automotive parts and medical devices [7].

Optimising an unknown material for LS requires characterisation of both extrinsic and intrinsic properties that are relevant to the LS process, such as bulk powder flow efficiency, melt and re-crystallisation temperatures and laser absorption capabilities [8]. The distribution of different sized particles within a sample affects both flow and packing efficiency, which in turn can increase porosity in the end-use part, and subsequently reduce mechanical strength. Tiwari *et al* [9] define the ideal Particle Size Distribution (PSD) for polymer materials as 50-90µm, although it is suggested that a binomial PSD may result in greater packing efficiency; the idea being that the smaller particles would effectively fill-in gaps between larger particles. Ziegelmeier *et al* [10] performed several experiments to investigate the effects of individual particle and bulk powder characteristics relating to the LS process. They describe in detail how they used a selection of specialised laboratory equipment to establish a valid experimental framework, and the same group re-applied this methodology in later work to determine the effects of particle and bulk powder characteristics on the mechanical properties of end-use parts [11].

A highly spherical particle morphology is desired for LS, as irregular shaped particles flow less efficiently due to mechanical interlocking and friction, effectively making the sample more cohesive [12]. Particle morphology is usually determined by the method used to create the powdered material; precipitation is an effective way to create spherical particles, but is not applicable for many materials. TPU, for example, is often cryogenically fractured, which results in irregular, non-spherical particles [13]. There are numerous external factors that may increase cohesiveness within a sample, such as moisture or static electricity, and this is often related to the method of storage, but can be material specific also. Researchers have investigated methods to effectively decrease cohesiveness, including pre-processing treatments and lubricating additives [14].

Understanding the thermal properties of a material is essential in LS, as they allow the user to determine the optimal processing parameters [15]. During LS, material is heated to a point slightly below melting temperature (T_m), which reduces the amount of laser energy required to achieve fluidity and allow consolidation. After consolidation, the material cools and re-crystallises as it reaches peak crystallisation temperature (T_c); the phase between T_m and T_c is known as the 'sintering window'. Most researchers use Differential Scanning Calorimetry (DSC) to obtain an estimate peak temperature for both states [16]. For polymers, it is necessary to have a wide sintering window, as a narrow window requires very specific system parameters that are often difficult to achieve and maintain throughout a build. If T_m and T_c peaks are close together, the material will rapidly cool soon after melting and cause shrinkage/distortion. DSC can also give information regarding glass transition temperatures [17].

In this study, an unknown grade of TPU will be characterised and optimised for use in a desktop-LS system. Successfully manufactured parts will be submitted to a variety of mechanical tests, and compared to commercially available, industrial grade TPU materials.

Methods

Desktop-Laser Sintering System

For this study, a Sintratec Kit (*Sintratec AG*, Switzerland) was purchased and assembled according to manufacturer guidelines. The Sintratec Kit is a commercially available desktop-LS system that has a build chamber volume of 110mm x 110mm x 110mm, and can reach temperatures up to 180°C. The system uses a blue laser diode, rather than CO_2 or Nd:YAG that are common in industrial LS systems. This means that there are material limitations to consider when using this system (see below).

Materials

The grade of TPU used here (UNEXTPU, *Dakota Coatings*, Belgium) has, to the authors knowledge, not yet been used in LS. The advertised application for UNEXTPU is a '*Transfer Powder*', which improves adhesion of lettering to sportswear. A carbon additive was required to facilitate laser absorption during LS processing, and so graphite was chosen due to its proposed absorptive and lubricating effects [18]. Materials were mixed manually to form the bulk powder (hereafter referred to as UNEXTPU-G). Nylon PA12 was provided with the Sintratec Kit, and is considered a known powder for this system; therefore, it was analysed alongside the unknown material during powder characterisation to act as a benchmark. After initial characterisation and LS, unfused powder samples were retained to determine the level of recyclability; samples recycled once (UNEXTPU-G-R1) and twice (UNEXTPU-G-R2) consisted of 100% used powder i.e. no 'virgin' UNEXTPU-G was added.

Material Characterisation

Particle Size Distribution

PSD of UNEXTPU was analysed by Laser Diffraction using a Mastersizer3000 (*Malvern Instruments*, UK). Feed rate: 15%; Air pressure: 2.2 barg; Opaque setting.

Particle Morphology

UNEXTPU and UNEXTPU-G samples were imaged by optical microscopy using an Eclipse LV100ND microscope (*Nikon*, Japan). General observations concerning particle morphology and graphite-coating were made.

Ultraviolet–visible Spectroscopy

As mentioned, the Sintratec Kit uses a blue laser diode, and so materials that are unable to absorb light at 445nm require a carbon additive to facilitate absorption. Ultraviolet-visible spectroscopy (UV-vis) was used to determine the amount of carbon additive required to make UNEXTPU-G viable at 445nm. Analysis was performed using a Varian Cary 300 Bio UV-Vis spectrophotometer (*Agilent Technologies*, USA). PA12 was analysed, and UNEXTPU-G samples with similar absorptive properties were considered viable.

Flow Efficiency

Dynamic bulk powder characteristics were analysed using a FT4 Rheometer (*Freeman Technology*, UK). The *Stability and Variable Flow Rate* test uses a specially designed helical blade attachment, which is driven through the sample in a downwards motion. The blade is sensitive to resistance in the sample, and returns data relating to the *Total Energy (mJ)* required for efficient powder flow. In this analysis, a lower *Total Energy* score equates to a higher flow efficiency, and *vice-versa* [19]. Initially, UNEXTPU, UNEXTPU-G and PA12 were analysed

for comparison; later, samples of UNEXTPU-G-R2 were also analysed to test for changes of flow efficiency in recycled powder.

Thermal Analysis

DSC analysis of UNEXTPU was performed on a Q2000 Differential Scanning Calorimeter (*TA Instruments*, USA). 7.2mg samples were prepared in an aluminium crucible; Nitrogen Atmosphere; Range: -20 - 200^{o}C; Rate: 10^{o}C/min.

Mechanical Testing

Tensile Testing

Test specimens were manufactured in a XY orientation following ATSM D638 Type V standards. Specimens were manufactured using UNEXTPU-G, UNEXTPU-G-R1 and UNEXTPU-G-R2. Testing was performed using a 5980 Floor Model (*Instron*, UK). Temperature: 18^{o}C; Humidity: 50%; Extension: 50mm/min.

Shore (Durometer) Hardness

Test specimens were manufactured in a XY orientation following ATSM D2240 Type A standards. Specimens were manufactured using UNEXTPU-G, UNEXTPU-G-R1 and UNEXTPU-G-R2. Testing was performed using a Type A Durometer (*Coats*, UK). Configuration: 35^{o} truncated cone; Diameter: 1.4mm; Extension: 2.54mm; Spring Force: 8.06N.

Statistical Analysis

Statistical analyses were performed using SPSS v22 (*IBM*, USA.). One-way analysis of variance (ANOVA) was performed for *Total Energy* data with a 95% confidence interval. Post-hoc *Bonferroni* analysis was applied, and a corrected *P* value of <0.05 was significant.

Results

Material Characterisation

Particle Size Distribution

UNEXTPU was analysed using Laser Diffraction to determine PSD (Fig. 1). UNEXTPU has an advertised PSD of 80-200µm; however, the analysis found that the actual PSD is slightly wider. It was decided that bulk powder samples would be manually sieved through a 300µm sieve before LS. D10: 120µm; D50: 180µm; D90: 275µm.

Particle Morphology

Samples of UNEXTPU and UNEXTPU-G were examined using optical microscopy, and images can be viewed in figure 2. UNEXTPU particles appear to be relatively non-spherical, which could potentially have a negative effect on flow and packing efficiency during LS. Graphite particles had clearly adhered well to the surface of UNEXTPU particles, proving that manual mixing was effective in this case.

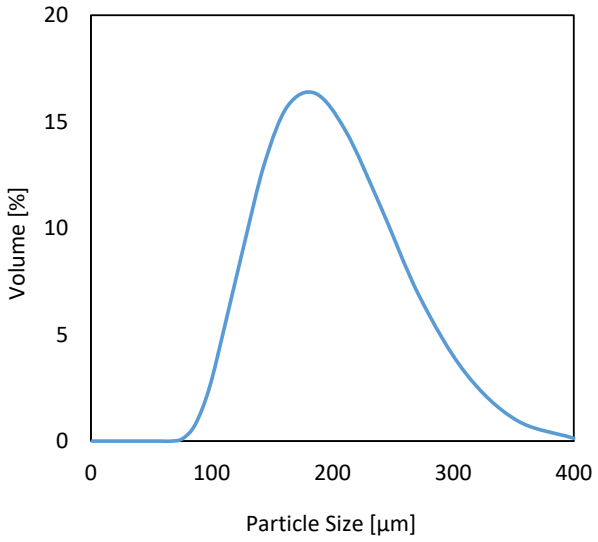

Figure 1. *Particle Size Distribution data for UNEXTPU [n=5].*

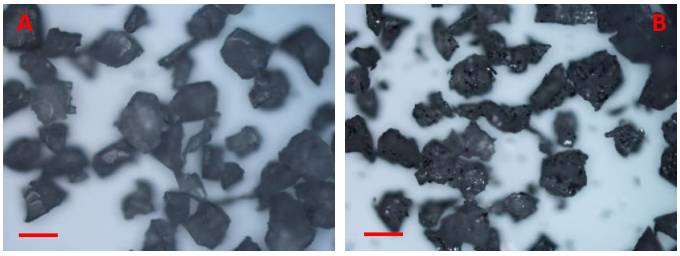

Figure 2*. Optical images of UNEXTPU [A] and UNEXTPU-G [B]. Scale: 200um*

Ultraviolet–visible Spectroscopy

UV-vis spectroscopy was used to determine the amount of graphite additive required to facilitate 445nm wavelength absorption in UNEXTPU. Several different samples ranging from 1% to 50% graphite additive were analysed along with UNEXTPU and PA12, and results can be viewed in figure 3. At 445nm, 2%, 3% and 4% graphite-UNEXTPU samples possessed similar absorption properties to PA12. To minimise any potential negative effects of the graphite, the lowest amount of additive required was preferred for part manufacturing; in this case, 2%.

Flow Efficiency

Bulk powder flow efficiency was investigated using a FT-4 Rheometer. Samples of UNEXTPU, UNEXTPU-G, UNEXTPU-G-R2 and PA12 were analysed using the *Stability and Variable Flow Rate* test, and *Total Energy* results can be viewed in figure 4. PA12 bulk powder flow was highly efficient when compared to UNEXTPU, which required approximately 8-times *Total Energy*. This is likely explained by the difference in particle morphology between the two materials; PA12 particles are highly spherical in comparison to UNEXTPU. The addition of 2% graphite (UNEXTPU-G) resulted in a significantly more efficient bulk powder flow compared to UNEXTPU ($P<0.05$). This is evidence for the lubricating effect of graphite. Flow efficiency remained unchanged in UNEXTPU-G-R2 when compared to UNEXTPU-G, meaning that the LS process does not affect bulk powder flow efficiency in any way.

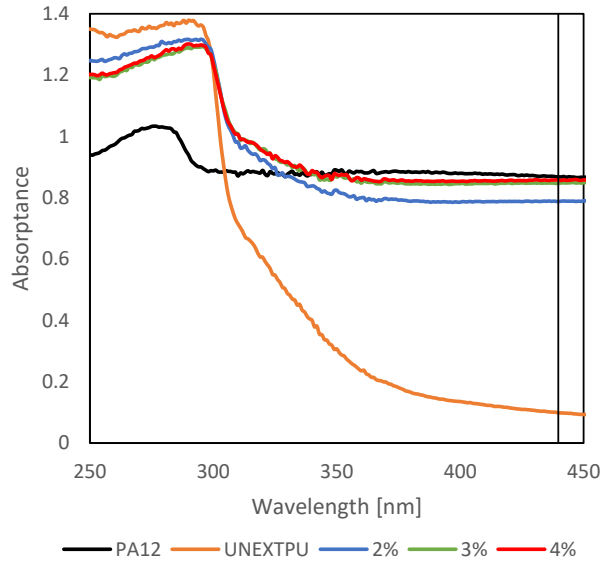

Figure 3. *UV-vis data [n=5]. Data between 5%-50% excluded for visualisation purposes. Vertical line indicates 445nm.*

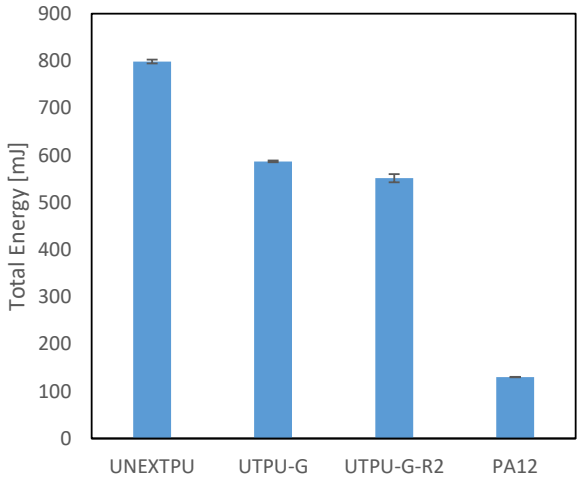

Figure 4. *Total Energy (flow efficiency) data [n=5]. Mean ±SE.*

Thermal Analysis

Samples of UNEXTPU were analysed using DSC, and results can be viewed in figure 5. The datasheet provided with UNEXTPU states that the onset of melting begins at 128°C and peak T_m is at 144°C. DSC analysis found that the onset of melting happens at a lower temperature of 119°C, but peak T_m was accurate at 144°C. The sintering window is wide, with a difference of 96°C between peak T_m and T_c, which suggests that UNEXTPU is suitable for LS. Based on DSC results, the powder bed temperature should be set at approximately 117-118°C.

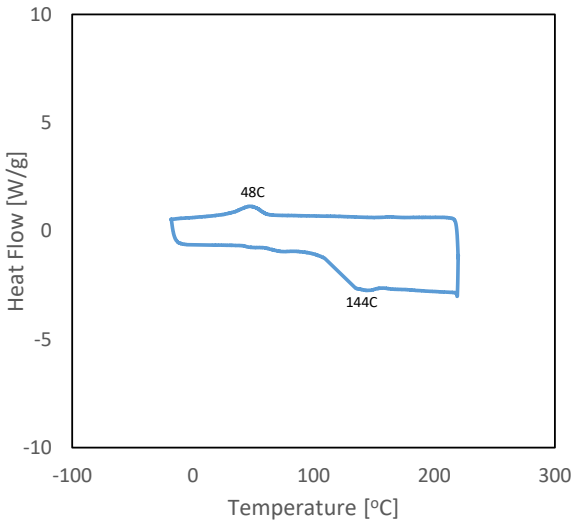

***Figure 5**. DSC data for UNEXTPU. Peak T_m and T_c displayed; sin-window = 96C.*

Desktop-Laser Sintering

Material characterisation enabled preliminary system parameters to be established. First, parts with simple geometric designs were manufactured, to verify that UNEXTPU-G could be processed in the *Sintratec Kit*. After initial testing, more complex geometries were processed to enable fine tuning of system parameters (Fig. 6). Depending on the surface area of a specific layer within a design, inconsistent powder bed heating throughout the build chamber caused the scan profile to bleed, and ultimately lose resolution when exposed for longer periods of time. Empirically altering scan speed layer by layer depending on cross sectional area was operator intensive and inaccurate. When processing consistent layer geometries, for example, tensile specimens (see below), optimum parameters were easily achieved. System parameters used for mechanical-test parts can be viewed in table 1.

Mechanical Properties

Tensile Testing

UNEXTPU-G, UNEXTPU-G-R1 and UNEXTPU-G-R2 test specimens were manufactured following ATSM D638 Type V standards. Ultimate Tensile Strength, Tensile Modulus and Elongation at Break remained consistent in UNEXTPU-G and both recycled samples (Figs. 7, 8, 9). Properties are comparable to industrial grade TPUs, except for Elongation at Break, which is relatively low (Table 2).

Shore (Durometer) Hardness

UNEXTPU-G, UNEXTPU-G-R1 and UNEXTPU-G-R2 test specimens were manufactured following ATSM D2240 Type A standards. Shore Hardness remained consistent in UNEXTPU-G and both recycled samples (Fig. 10) and is comparable to industrial grades also.

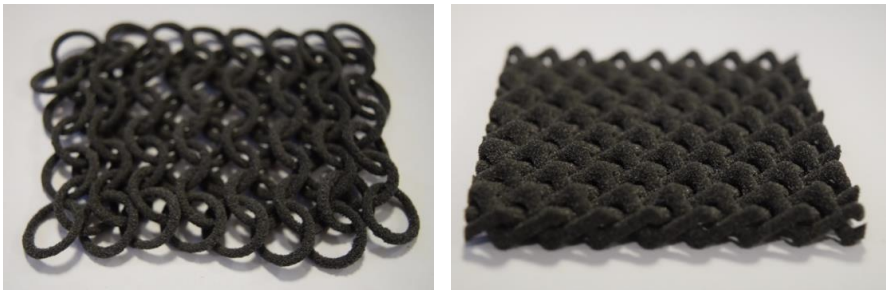

***Figure 6**. Complex geometrical parts manufactured in the Sintratec Kit. Images: FS.*

***Table 1**. Desktop-LS system parameters used to create tensile/shore hardness specimens.*

Parameter	Value
Laser Power [W]	3.2
Scan Speed [mm/s]	200
Hatch Spacing [µm]	150
Layer Thickness [µm]	200
Chamber Temperature [ºC]	96
Bed Temperature [ºC]	117

***Table 2.** Compartive mechanical data. Data sourced from technical data sheets available online.*

Material	Ultimate Tensile Strength	Tensile Modulus	Elongation at Break	Shore Hardness
UNEXTPU-G	7.9	48.7	139	75
DuraForm® Flex	1.8	7.4	110	45
LUVOSINT X92A-1	20	-	520	92
Materialise TPU92A	27	-	400	92
AMLLC FLEX TPU	-	40	300	81
PRODWAYS TPU	7	65	350	70
Rowak AG Rolaserit®	7	55	350	70
FIT Elastomer TPU	5.5	65	200	-

*Ultimate Tensile Strength [Mpa]; Tensile Modulus [Mpa]; Elongation at Break [%]

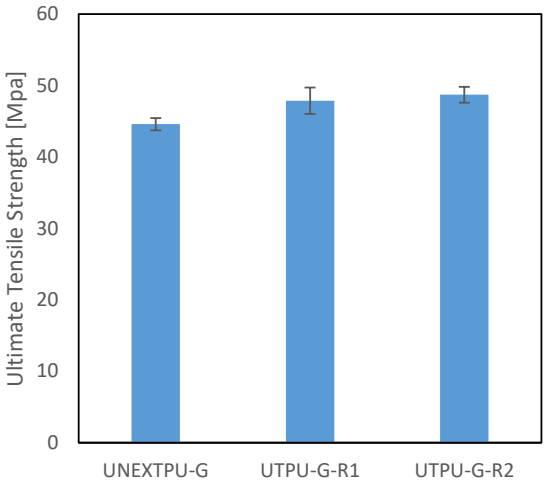

***Figure 7**. Ultimate Tensile Strength data [n=5]. Mean ±SE.*

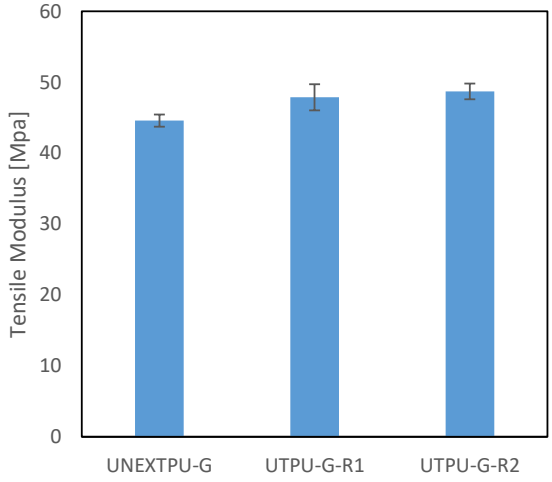

***Figure 8.** Tensile Modulus data [n=5]. Mean ±SE.*

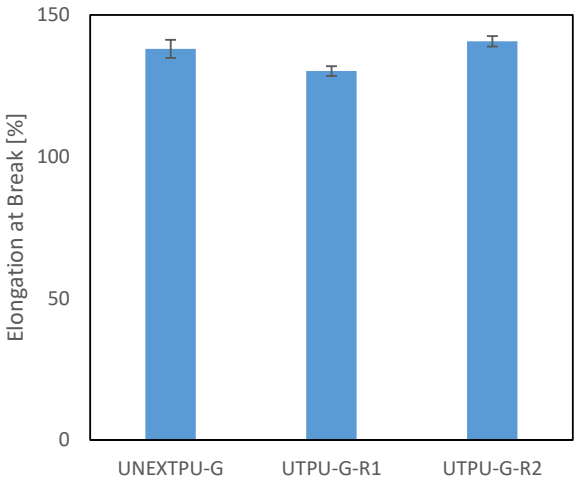

***Figure 9**. Elongation at Break data [n=5]. Mean ±SE.*

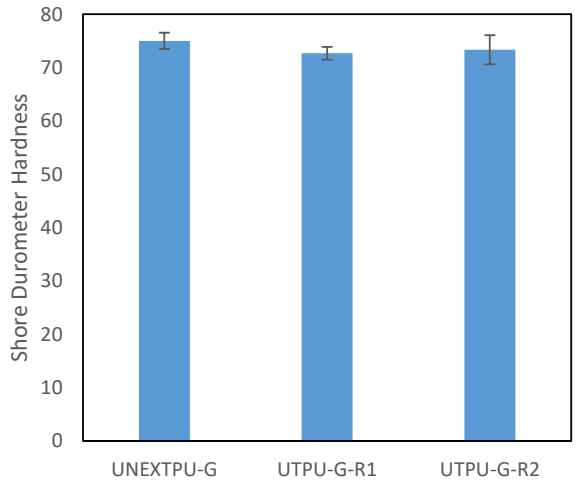

***Figure 10**. Shore Durometer Hardness data [n=3]. Mean ±SE.*

Discussion

In this study, a previously unknown grade of TPU has been successfully optimised for desktop-LS, and a much-needed new material option has been established for this AM process. Desktop-LS systems are a relatively recent introduction to the AM market, but they potentially offer a much more robust and sophisticated alternative to the widely available Material Extrusion systems, that have been accessible for some time. There is great market potential for elastomeric materials, and so the ability to produce end-use parts that are geometrically complex, mechanically proficient and relatively inexpensive is an attractive prospect to industry and small business owners alike [6].

The recyclability of UNEXTPU is a huge positive in terms of manufacturing costs which, despite the proposed economic potential of AM, remains an issue in some processes, as the cost of materials can be relatively high [6]. Only once and twice recycled powder were analysed in this study and, ideally, more will be investigated in future work; however, the reduction in costs associated with re-using material twice is economically beneficial, especially as no 'virgin' powder was required to maintain mechanical properties in the end-use parts. Usually, in LS, a certain amount of unused material is required to facilitate further processing [20]. UNEXTPU is also relatively inexpensive; at the time of writing, the cost is approximately 26GBP/kg (~34USD; ~30EUR). The cost of the carbon additive was minimal, and very little was required to facilitate LS.

Material characterisation was successful for the most part; UV-vis was effective in establishing the required amount of carbon additive, and there was also a significant associated lubricating effect that greatly improved bulk powder flow efficiency. It could be argued that the *Total Energy* data output from the FT4 Rheometer is somewhat arbitrary, as it is difficult to define what is being recorded during the analyses; however, for comparing samples contained within a single experiment, it remains quite useful. No analysis of sphericity was made, but this characteristic cannot be affected in any way post-powder manufacturing i.e. there is no realistic, inexpensive way to make individual particles 'more' spherical. Optical microscopy was effective for establishing that graphite was well-adhered to TPU particles, and thermal analysis allowed for an adequate LS temperature to established.

The PSD of UNEXTPU is much wider than the proposed ideal range for polymers (50-90µm), yet the mechanical properties remain comparable to industrial grade TPUs. This means that either Tiwari et al [9] have underestimated the ideal range, or that there is potential for improving the mechanical properties of UNEXTPU even further. UNEXTPU is also available with an advertised PSD of 0-80µm which could be useful in future investigation of this material; a 50µm sieve could be used to bring the sample closer to the proposed ideal range, or both 0-80µm and 80-200µm could be combined in specific ratios to form a binomial PSD. The latter would make for an interesting study; analyses for flow and packing efficiency could be supported by porosity and mechanical testing across a variety of binomial PSDs.

Finding the optimal system parameters for more geometrically complex parts was difficult, and required manual adjustment throughout the build, which is not ideal, as AM is supposed to be a largely automated process. Relatively simple, geometrically uniform parts (such as those used for mechanical testing) required no adjustment during builds, and there appeared to be no difference between parts in terms of geometrical accuracy and mechanical properties, regardless of their position in the build area. However, the effects of part positioning throughout the entire build volume should be investigated more thoroughly, as poor

temperature regulation is a common issue in LS systems [21]; indeed, there was some degree of delamination observed during commissioning of the Sintratec Kit, particularly in parts positioned in the front left and right corners of the build area.

Tensile testing and shore hardness were analysed in this study, and both are significant for TPU as many of the proposed applications of elastomeric materials rely on high elasticity, and some resistance to plasticity. 'Shape memory' is desirable; whether under compression or tension, manufacturers require materials that will maintain their original shape after extended periods of use, and thus retain an adequate shelf-life [22]. Therefore, a logical next step when investigating the mechanical potential of UNEXTPU is to perform experiments designed to test shape memory under conditions of prolonged tension, compression and perhaps a variety of environmental factors, such as temperature and humidity [23].

Conclusion

This aim of this study was to introduce a previously unknown material for desktop-LS, as current desktop systems are extremely limited by their material choice. It is reasonable to suggest that the aim of this study was met, and that UNEXTPU is now a viable and relatively inexpensive option for desktop-LS; however, there remains a need for future research to determine optimal processing parameters and the mechanical potential of this material. Application-specific research is also encouraged, as TPU has excellent market potential.

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