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Tools to Define and Evaluate Morphology Mapping, A Route to Complex Structures Using Direct Digital Manufacturing

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Abstract. Direct Digital Manufacturing is a new set of technologies which allow objects to be printed directly from a digital definition. Such technologies allow us to manufacture any self-supporting shape, but simply replicating shape is not sufficient for the production of many parts especially those with specific function. We need to be able to generate complex multiscale structures similar to those we observe in nature. Direct digital manufacturing can be seen as method for achieving this, as we can deposit materials with different compositions and different structures in selected volumes and thereby generate a complex structure. This manuscript addresses the challenges of achieving this concept and the tools needed to characterize the parts produced and the variation in the composition and structure. We conclude by discussing how we might design such complex parts.

INTRODUCTION

Direct digital manufacturing is a rapidly growing area which is building on the successes of layer by layer rapid prototyping technologies [1] by working with improved materials to yield products with good properties. There are a variety of build technologies which are current under intense development [2]. In this work, we focus on just one, fused deposition modelling [3], but the general principles of our approach may be applied to other build technologies. Our objective is to be able to use direct digital manufacturing technologies which are able to successfully build objects with a complicated spatial variation in the composition, structure and morphology and hence properties in a digitally defined manner. Such objects are expected to exhibit properties which are different to the parent polymers. To achieve this objective we need to be able to produce regions with different compositions, structure and morphology in a reliable and consistent manner and characterise this complexity and we need to be able to design this level of complexity as part of the digital definition of the object. Although there are many build technologies which could be used we have selected fused deposition modelling using a conventional thermoplastic, as the focus in this work.

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FUSED DEPOSITION MODELLING

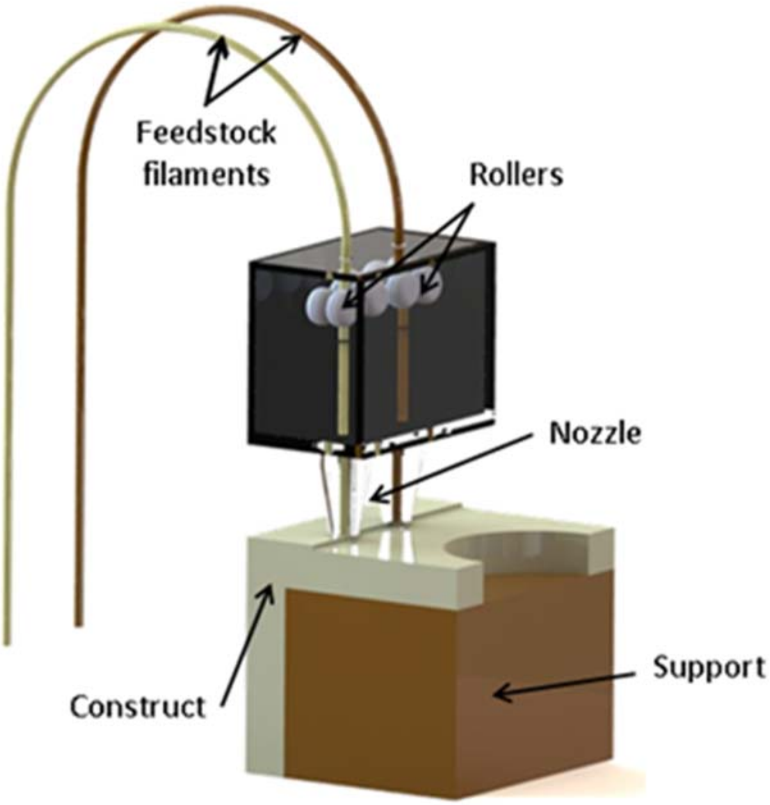

FIGURE 1. A schematic of the Fused Deposition Modelling Technology

Figure 1 shows the basic elements of the fused deposition modelling technology. Essentially pre-formed polymer filaments are fed in to a small heated extruder from which a liquid strand emerges from and is deposited on to a moving build platform. The liquid strand cools and becomes solid as a consequence of vitrification in the case of amorphous polymers or through crystallisation for semi-crystalline polymers. The time taken for solidification will have a major impact on the build quality as during the liquid state, the polymer can change shape or position from the deposited condition.

PROCESSING PARAMETERS

As with all polymer processing, the conditions using in the FDM process will have a profound effect on the solid state structure and morphology of the polymer deposited on to the build platform. In this work we are using poly(€-caprolactone) with a MW of 80,000 Daltons(Supplied by the Aldrich Chemical Company) which melts at 60°C and which starts crystallising at ~36°C. As a semi-crystalline polymer, the time-temperature profile is a critical parameter of the processing (4). Other key parameters are the extrusion rate, the relative velocity between the print head and the build platform and the geometric parameters such as the diameter and length of the extrusion port. A straightforward method of characterising the structure and morphology of the extrudate is small-angle x-ray scattering (5). The extrudate is ~ 300µm in diameter. We have used the NCD-SWEET beamline at the ALBA synchrotron light source in Barcelona, Spain for this purpose. The beamline was setup with the incident wavelength of 1Å. Figure 2 shows SAXS patterns of PCL Extruded filaments measured at room temperature and prepared using a melt reservoir temperature of (a) 80°C, and (b)) 120°C. Filaments prepared at the lower temperature show a highly anisotropic small-angle x-ray scattering pattern, while the filaments prepared at the higher temperature display a virtually isotropic pattern. We can quantitatively evaluate the level of preferred orientation using a rigorous approach developed by Mitchell and co-workers (6).

SMALL-ANGLE X-RAY SCATTERING AND PREFERRED ORIENTATION

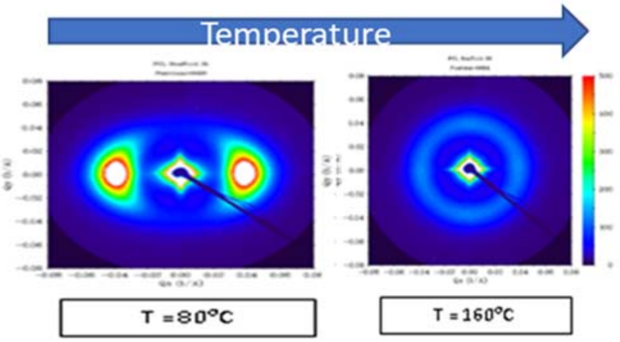

FIGURE 2. SAXS patterns recorded for filaments prepared with melt reservoir temperatures indicated. The filament strand alignment is vertical on the page

We shall be concerned with the single elastically scattered x-ray intensity $I(|\underline{Q}|, \alpha)$ from a sample with uni-axial symmetry where $|\underline{Q}|=4\pi\sin\theta/\lambda$ with 2θ as the scattering angle, λ the incident wavelength and α the angle between the scattering vector $\underline{Q}$ and the symmetry axis of the sample.

The scattering for a sample exhibiting a partial level of preferred orientation can be written as the convolution of the scattering for a perfectly aligned system $I^0(|\underline{Q}|, \alpha)$ with the orientation distribution function $D(\alpha)$:

$$I\left(|\underline{Q}|,\alpha\right)=I^0\left(|\underline{Q}|,\alpha\right)*D\left(\alpha\right) \tag{1}$$

The function $D(\alpha)$ describes the distribution of the structural units with respect to the symmetry axis of the sample. If we express the intensity functions and the orientation distribution function in terms of a series of spherical harmonics, $I_{2n}(|\underline{Q}|)$, $I^0_{2n}(|\underline{Q}|)$ and D_{2n} we can write this convolution as [6-10]:

$$I_{2n}(|\underline{Q}|)=\left\{\frac{2\pi}{(4n+1)}\right\}D_{2n}I^{0}_{2n}(|\underline{Q}|),\alpha) \tag{2}$$

where $n=0,1,2,3\ldots\infty$. Only the even terms of each series are required due to the inversion centre intrinsic to a x-ray scattering pattern for a non-absorbing sample. The components of each series can be obtained by:

$$I_{2n}(|\underline{Q}|)=(4n+1)\int_{0}^{\pi/2}I\ \ (|\underline{Q}|,\alpha)P_{2n}(\cos\alpha)\sin\alpha.d\alpha \tag{3}$$

and related expressions. The complete scattering pattern may be recovered by:

$$I(|\underline{Q}|,\alpha)=\sum_{2n=0}^{2n=\infty}I_{2n}(|\underline{Q}|)P_{2n}(\cos\alpha) \tag{4}$$

The value of this representation in terms of spherical harmonics is that the effects of preferred orientation are separated from the dependence of the observed scattering on the spatial correlations. Equation 2 underlines that for samples with the same structure, the variation of the amplitudes of the spherical harmonics $I_{2n}(|\underline{Q}|)$ with $|\underline{Q}|$ are essentially the same, with a simple constant multiplier dependent on the level of preferred orientation. This observation is the basis of a wide-angle x-ray scattering based conformational analysis procedure developed for disordered polymers 7].

The orthogonal nature of the spherical harmonic functions in equation 3 means that for a multiple phase structure in which the scattering is additive, the resultant spherical harmonics will also be linear combinations of the harmonic functions for each phase. We can write:

$$I_{2n}(|\underline{Q}|) = xI_{2n}^{a}(|\underline{Q}|) + (1-x)I_{2n}^{b}(|\underline{Q}|) \tag{5}$$

where $I^{a}_{2n}(|\underline{Q}|)$ are the spherical harmonics for the pure phase. Combining equation 6 with 3 we can write more completely:

$$I_{2n}(|\underline{Q}|) = xI_{2n}^{0a}(|\underline{Q}|)D_{2n}^{a}\frac{2\pi}{4n+1} + (1-x)I_{2n}^{0b}(|\underline{Q}|)D_{2n}^{b}\frac{2\pi}{4n+1} \tag{6}$$

where $I^{0a}_{2n}(|\underline{Q}|)$ are the functions for the pure perfectly aligned phase. For a particular experimentally observed harmonic equation 7 reduces to:

$$I_{2n}(|\underline{Q}|) = k_{2n}^{a}I_{2n}^{0a}(|\underline{Q}|) + k_{2n}^{b}I_{2n}^{0b}(|\underline{Q}|) \tag{7}$$

where k_a and k_b are scaling constants with k_a given by

$$k_{2n}^{a} = xD_{2n}^{a}\frac{2\pi}{4n+1} \tag{8}$$

and k_b by a similar expression. Equation 8 provides a route to the separation of the scattering into the contributions from each phase. We simply need a mechanism to identify the components within each 1-d function. There is considerable advantage in using information from the scattering patterns of the pure phases where this is available. Although such scattering patterns need to arise from samples with the same structure, it is not necessary for the level of preferred orientation to be the same. As emphasised above the variation of the harmonic function with $|\underline{Q}|$ does not depend, other than through a simple constant, on the orientation. This allows information from partially oriented samples to be used as "standards" in the separation and analysis. The process of separation is then a simple numerical fitting process. Moreover, since such processes are performed in the more straightforward environment of 1-d functions, rather than directly on the original 2-d patterns, there is a considerable gain in simplicity. It is also possible to use calculated curves from atomistic or analytical models as the base functions. Of course fundamental to this analysis is that the scattering only arises from the components we are seeking to evaluate. Any instrumental background, for example the dark signal from a CCD based detector, must be subtracted prior to any analysis.

In the description of the levels of preferred orientation, it is convenient and conventional to work with normalised spherical harmonics $< P_{2n}(\cos\alpha) >$ [6]. The harmonic $<P_2(\cos\alpha)>$ is often referred to as the "Hermans orientation function" in the field of polymers or the "order parameter" in the context of liquid crystals; for perfect alignment $<P_2(\cos\alpha)> = 1.0$ and for a random or isotroptic distribution $<P_2(\cos\alpha)> =0$. The normalised functions are defined as [6]:

$$< P_{2n}(\cos\alpha) > = \frac{\int_0^{\pi/2} D(\alpha)P_{2n}(\cos\alpha)\sin\alpha.d\alpha}{2\pi\int_0^{\pi/2} D(\alpha)\sin\alpha d\alpha} \tag{9}$$

Such normalised orientation parameters can be obtained from the scaling constants in equation 9:

$$< P_{2n}^{a} \cos(\alpha) >= \frac{k_{2n}^{a}}{k_{0}^{a}} = \frac{D_{2n}^{a}}{D_{0}^{a}(4n+1)} \tag{10}$$

Alternatively we can obtain the numerical values of these orientation parameters from the extracted spherical harmonic functions using:

$$< P_{2n}^{a} \cos(\alpha) >= \frac{I_{2n}^{a}(|\underline{Q}|)}{I_{0}^{a}(|\underline{Q}|)(4n+1)P_{2n}^{m}(\cos\alpha)} \tag{11}$$

where $P_{2n}^{m}(\cos\alpha)$ are normalised coefficients which describe the scattering for a perfectly aligned sample [6]. For a set of lamellar crystals the values of P^{m}_{2n} are 1.0, although there made some adjustment for the instrumentation and resolution of the system. Values will depend upon the particular structural feature and hence are in part Q dependent. For an *hk0* Bragg reflection the value of $P_{2}^{m}(\cos\alpha)$ =-0.5, while for a meridional feature $P_{2}^{m}(\cos\alpha)$ = 1.0 [6]. Equation 12 represents a more generalised approach which can be used with any set of extracted spherical harmonic functions. For example, we will use this equation in the example below, as the base functions from the fully aligned pure samples required for the implementation of equation 11 are not available. Such base functions may be obtained from experiment or through from models. Equation 12 may also be used in situations where the separation inherent in equation 8 has been performed using a peak fitting approach based on differing peak shapes, for example, as appropriate for crystalline and amorphous phases. Using this methodology the levels of preferred orientation of the lamellar crystals as measured from the SAXS patterns shown in Figure 2 are $<P_2>=0.81$ for T=80°C and $<P_2>=0.04$ for T=120°C.

PROPERTIES

The different levels of preferred orientation of the lamellar crystals in the PCL filaments prepared using the different processing parameters shown in Figure 2 lead to a variation in the modulus of the filaments by a factor of 2. This has allowed us to develop a methodology to print samples with different mechanical properties in specific areas of the sample. The Intrinsic connectivity of the strand minimises the area of interfaces introduced during the build process which could lead to product failure. The question arises as how to design such a material. We are exploring the use of the so-called reverse Monte-Carlo methodology (12) to design such materials.

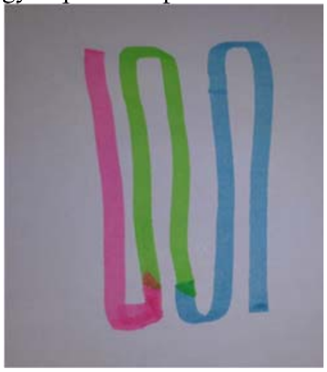

FIGURE 3. A schematic of a polymer strand produced using different processing parameters as indicated by the different colours

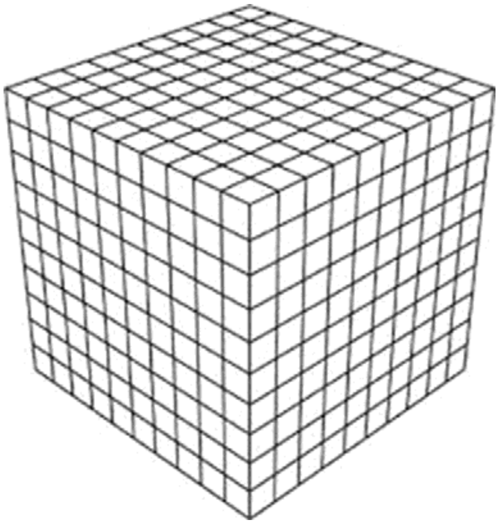

FIGURE 4. The 3d grid sued to define the process parameters for each volume of the material

The digital design involves defining the process parameters for each volume element of total build volume. The use of different processing parameters in each volume elements leads to a variation in the structure and morphology of the material as shown in Figure 3. We know select an element at random and adjust the values of the processing parameters using carefully selected increments and calculate the mechanical properties of the object. If this adjustment leads to an improved fit to the target properties then the adjustments are accepted. We evaluate this via a χ^2 test

$$\chi^2 = (Y_{obs}^2 \text{-} Y_{target}^2)/\sigma^2$$

Where σ is the standard deviation in the experimental data point Y_{obs}. If we wish to use a stress-strain curve to define the properties we can sum over a series of points (T_{arget}) that define that curve. If χ^2 is not reduced then a metropolis type test is used to evaluate whether the modifications are to be accepted with Probability

$$P = \exp(-\Delta\chi^2/2)$$

This test ensures that the system does not get trapped in a local minimum but quickly reaches a global minimum. We repeat this process many times until there is convergence in the target function of the desired mechanical properties. The methodology although apparently simple has firm foundations in statistical mechanics and can be seen as a development of the Metropolis–Hastings algorithm (13) which is essentially a Markov chain Monte Carlo method for obtaining a sequence of random samples from a probability distribution from which direct sampling is difficult. Under certain circumstances it can be shown that it leads to the correct analytical solution. Of course the sampling can be fraught with correlation. The stochastic nature of the changes means that the resultant variation in properties and process parameters is the most random that delivers the property required.

CONCLUSIONS

We have shown that we can use the standard fused deposition modelling direct digital manufacturing technique to prepare difference regions of the same object with different properties. Small-angle X-ray techniques can be used to quantitatively evaluate the level of preferred orientation of the chain folded crystalline lamellar crystals. We show how an approach based on an expansion of the data in a series of spherical harmonics lead directly to an unambiguous evaluation of the preferred orientation. We describe how we can exploit inverse modelling techniques such as reverse Monte Carlo modelling to define the microstructure needed to deliver a meta material with specific properties. It is clear that this technology has considerable scope for development and expansion.

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