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Fire resistance of additively manufactured water filled polymer parts

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ABSTRACT

This paper introduces the concept of additively manufactured (AM) water filled parts (WFPs). By combining the energy absorbing properties of water with polymers, it is possible to significantly improve the time to ignition of AM parts with open internal structures. Theory relating the flame temperature to the maximum wall temperature of WFPs is developed. A range of water-polymer configurations are presented as a basis for WFP designs. Three separate thermal experiments were conducted to test different aspects of the WFPs. The time to ignition for cone calorimetry samples was extended 794% over plain photopolymers. Case studies were used to demonstrate the effectiveness of WFPs with complex shapes. The results of thermo-fluid finite element simulations showed good agreement with experimental observations and provide a useful tool for the evaluation and optimisation of WFP designs. The fire resistance of thin walled structures with internal water volumes was found to be significantly improved. The water filling strategy was found to be more effective than adding intumescent coatings. Finally further work and recommendations are discussed.

1. Introduction

1.1. Background

An important consideration for the use of additively manufactured (AM) polymers in high fire risk areas, is the polymers flammability and heat strength [1]. Of the 345 polymers listed on Senvol's additive manufacturing database only eight are currently rated V-0, according to the UL 94 standard [2]. The V-0 rated polymers are either high performance plastics (PEEK, PEAK, PEI or PPSF) or contain chemical flame retardants. Processing polymers with high thermal performance, such as PEEK, are more expensive than polymers like PA12, due to higher material costs, higher processing temperatures and lower powder recyclability [3]. Polymers in general also suffer from fairly low heat deflection temperatures ranging from 38 to 263 °C at 0.45 MPa, a property not improved by adding flame retardants [2]. At 300-400 °C most polymers begin to decompose releasing flammable volatiles which add further fuel to flames [4-8]. There is extensive research aimed at improving the flame retarding properties of polymers. This is done in three main ways: (i) developing inherently flame retardant polymers, (ii) chemically modifying polymers and (iii) adding flame retardant particles to polymers [9]. Polymers with flame retardants often require high particle loadings, which can negatively affect the mechanical properties [10,11], reduce recyclability and introduce harmful chemicals, such as halogens, into the environment [12-14]. Polymers used in

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Received 6 March 2017; Received in revised form 4 April 2018; Accepted 9 April 2018 Available online 24 April 2018 2214-8604/ © 2018 Published by Elsevier B.V. AM have additional constraints when considering adding flame retardants, as processing often requires a very narrow range of stock material properties, such as powder flowability, particle size distribution, heat absorption, polymer viscosity and the stability of colloids or suspensions in photopolymer resins [15,16].

Another strategy to improve the fire resistance of polymers is to add a thermal barrier coating. A number of different coatings have been developed to insulate load-bearing substrates from fire using mineral refractories or intumescent materials [17]. They all function by forming a low density, air or gas-containing structure, which achieves its thermal resistance by immobilising the gas within it. The thermal conductivity of such structures is generally of the order of 0.01–0.05 W/ mK, regardless of the type of material [1]. While thermal barrier coatings are proven to be effective they are often not viable due to their added weight, low durability, appearance and solubility in water [18,19].

This paper presents a simple, effective and environmentally benign method for improving the fire resistance of AM parts, simply by filling them with water. These components will be referred to as water filled parts (WFPs). The concept is based on the well-known class room physics demonstration, where a paper bag is filled with water and placed over a flame. The paper does not burn, not because it is wet, but because the water absorbs the heat keeping the paper below its ignition temperature.

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Table 1

Thermal conductivities and specific heats of common materials [23-25].

Material	Thermal conductivity at 25 $^\circ\mathrm{C}$ (W/m K)	Specific heat capacity	
		(J/kg K)	(J/m ³ K)
PA 6	0.25	1600	1824
PLA	0.13	1800	2340
Air	0.024	1005	1231
Wood (oak)	0.17	2000	1833
Steel	43	490	3822
Aluminium	205	870	2484
Water	0.58	4182	4190
Concrete	1.7	880	2122

1.2. Water filled parts (WFPs)

The concept of improving fire resistance by filling structures with water is not new and has been applied to large steel structures [20,21]. Adding water to fire resistant fabric laminates has also been investigated via the addition of hydrogel layers [22]. This is believed to be the first study of its kind with a focus on the flame resistance of small complex polymer parts.

Polymers, with their low thermal conductivity and specific heat, result in materials with surfaces that can rapidly increase in temperature when subjected to a heat source, such as a flame. Table 1 provides thermal conductivity and specific heat capacity data for some common materials [23–25]. Note that water has a very high gravimetric and volumetric specific heat capacity. Water also has the benefit of being a fluid at room temperature, capable of high convective heat transfer rates and has a large latent heat of vaporisation. All of these properties make water an excellent choice to combine with polymers to improve the fire resistance of the printed parts.

Understandably, water cannot easily be mixed into the polymer before printing, so space must be made inside the part for the water at the design stage. Most polymer AM technologies are capable of producing hollow parts with open internal structures, that provide space for the water. For powder bed fusion, vat polymerisation and material extrusion methods these porous structures can then be filled with water in a post-build process and subsequently sealed (Fig. 1a). It may also be necessary to make the polymer part watertight before adding the water by coating with a sealant [26,27]. Material jetting technologies can be used to print the polymer and a non-curing liquid simultaneously, as demonstrated by MacCurdy et al. [28], avoiding the need for a two part process and allowing isolated and functionally graded internal volumes of liquid (Fig. 1b). For thick parts, where weight reduction is a concern a double shell structure can be used, as shown in Fig. 1c. If the surface of the part is likely to be damaged, then multiple shells may be added for redundancy. It is also possible to combine different strategies to find the right combination of strength, durability and weight.

Another important design consideration is the build-up of pressure within WFPs as the water is heated. Many polymers will soften sufficiently at 100 $^{\circ}$ C such that a thin wall (less than 1 mm thick) will leak at



Fig. 1. Cross sections of three water/polymer configurations: a) A hollow or open lattice structure filled with water, b) Functionally graded water volumes, c) double shell structure with water trapped between the inner and outer polymer shells.

relatively low pressures. For thick walled parts with softening temperatures over 100 $^{\circ}$ C, it may be necessary to include pressure relief points designed to preferentially vent when internal pressures start to rise above unsafe levels.

1.3. Heat transfer theory

Instantaneous heat transfer across a polymer wall, involves both convection and conduction as described by Eq. (1). As heat transfers through the wall the water will increase in temperature until it reaches 100 °C.

$$\dot{Q} = \frac{A}{\left[\frac{1}{h_h} + \frac{l_p}{k} + \frac{1}{h_c}\right]} (T_h - T_c)$$
(1)

A = the wall surface area, h_h = the effective convective heat transfer coefficient on the hot side, t_p = the wall thickness, k = the polymer conductivity, h_c = the convective heat transfer coefficient on the cold side, T_h = Temperature of the hot side, T_c = Temperature of the cold side.

The convective heat transfer coefficient on the water side is highly temperature dependant and varies between surfaces with different material combinations, surface roughness and local geometries. To simplify this problem the water can be assumed to be 100 °C until the water has completely converted to steam. The high temperature of the water is compensated for by the extremely high convective heat transfer rates present during boiling. If we assume there is an infinite supply of water to boil the problem becomes static, and the heat transfer and wall temperatures do not change with time.

The temperature of the wall surfaces is related to the temperature difference between the flame, water, and the heat flow as described by Eq. (2).

$$T_h - T_c = (T_h - T_{hw}) + (T_{hw} - T_{cw}) + (T_{cw} - T_c) = \frac{\dot{Q}}{A} \left[\frac{1}{h_h} + \frac{t_p}{k} + \frac{1}{h_c} \right]$$
(2)

where T_{hw} = the hot side wall temperature, T_{cw} = the cold side wall temperature.

Of critical importance is the maximum temperature of the polymer wall, T_{hw} . This can be calculated via Eq. (3) (see Appendix A for derivation).

$$T_{hw} = T_h - (T_h - T_c) / \left(\frac{h_h}{h_c} + \frac{t_p h_h}{k} + 1\right)$$
(3)

Assuming values for the heat transfer coefficients, polymer conductivity, flame temperature and water temperature, it is possible to investigate the effect of wall thickness and water temperature on the temperature profile across the polymer wall (Table 2).

The values for h_h and T_h were adopted from the work of Wang et al. [29,30] to represent the effective heat transfer coefficient and temperature of a flame consistent with UL 94 standards. The value for k was chosen as a generic mid-range value for polymers. A linear relationship for h_c was assumed, based on commonly quoted values for the convective heat transfer of water at 20 and 100 °C. Fig. 2 shows the temperature profile across polymer walls of varying thicknesses for a water

 Table 2

 Values used in Eqs. (1)–(3) to generate Figs. 2 and 3.

Parameter	Value	Units
$egin{array}{c} t_p & k & h_h & h_c & h_c & T_c & T_h & & \end{array}$	$\begin{array}{l} 0.5 \times 10^{-3} - 2 \times 10^{-3} \\ 0.2 \\ 54.3 \\ = 20(T_c) + 500 \\ 273 - 373 \\ 2026 \end{array}$	m W/mK W/m ² K K K
Α	1	m ²

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