

A Review of Selective Laser Sintering of Wood-plastic Composites

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Abstract

Eco-friendly wood-plastic composites were firstly proposed to be used as the raw materials of rapid prototyping in 2002, and successfully applied in Selective Laser Sintering (SLS) two years later. These composites were mixed by different kinds of wood powder, plastic powder and other additives. Different from polymer, ceramics, metals and their composites, wood-plastic composites are new types of sustainable and low-price feedstock of SLS.

This paper presents the development of the research of wood-plastic composites applied to SLS over the past decade. It contains the preparation and characterizations of wood-plastic composites, the study of temperature fields and molecular dynamics simulation of sintering wood-plastic composites, the effects of processing parameters on the forming accuracy and mechanical properties of sintered parts, and the post-treating process of wood-plastic composite parts. At last, it introduces the application fields of laser sintered wood-plastic composites parts.

Introduction

Selective laser sintering (SLS), one of 3D printing techniques based on additive manufacturing process, can directly produce geometrically complex components in layers from three-dimensional computer aided design (CAD) data without any special tooling or support structure [1]. In recent years, the SLS technology has witnessed rapid development in the areas of manufacturing industries, automobile, aerospace, and biomedical due to its superiorities of less waste, freeform and speedy fabrication [2]. During the SLS process, the model will be saved into STL file format and sliced into layers, and then the machine will use a CO₂ laser beam to selectively sinter each layer of powder material according to relevant slice information until finishing fabricating the product.

Theoretically, all kinds of powders which are fused by laser beam and solidify together quickly under certain process parameters can be used as SLS materials, and polymeric matrix, metallic matrix and ceramic matrix are the common SLS materials (David L. Bourell, Roadmap for Manufacturing, 2009). However, SLS material cost is

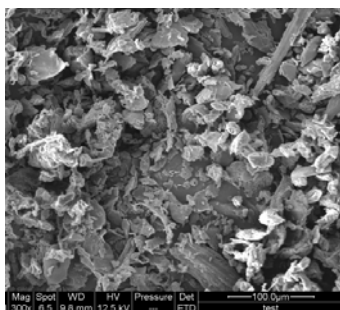
high [3] and there is a pressing need for the progression of SLS to extend the diversity of materials available especially sustainable and low-price ones [4].

This paper proposes wood-plastic composites (WPC) as the feedstock of SLS with the advantages of easy formability, environment-friendly concept, and low cost. Much work is done to study on SLS of WPC for getting a comprehensive performance evaluation of it, improving forming properties and accuracy of WPC used as SLS material. WPC composed of different types of natural fibers from agroforestry wastes, thermoplastic powders and additives is prepared for SLS. The laser sintering mechanism and interfacial bonding mechanism between fibers and plastic powders are explored by molecular dynamics simulation (MD), scanning electron microscopy (SEM) and fourier transform infrared spectrometer (FTIR). The factors of mechanical strength of sintered WPC parts are studied including material prescription, temperature field of sintering, process parameters and post-treating methods. As a result, the tensile strength and bending strength of sintered WPC parts are dramatically improved compared to those early results. The research on the forming accuracy of sintered WPC parts is made, and the results demonstrate WPC is a kind of high-precision SLS materials thus its SLS parts can be used as evanescent mode.

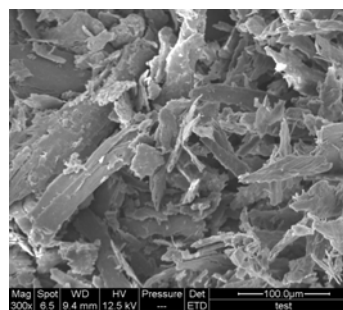
Preparation and laser sintering of WPC

2.1 Materials and Preparation of WPC

Wood powders are obtained by smashing agroforestry wastes into tiny particles with the particle diameter of less than 100 μ m. Five kinds of agroforestry wastes have been used as research objects of SLS including rice husk powder, cornstalk powder, pine powder, bamboo powder, eucalyptus powder and microcrystalline cellulose powder. Different kinds of wood powders have different morphological features as shown in Fig.1, however, their main components are cellulose, hemicellulose and lignin, which possess strong hydrophilicity and chemical polarity [5] compared to nonpolar thermoplastic polymers. Thus wood powders need to be alkali-treated and dried under the temperature of 102 $^{\circ}$ C to improve interfacial bonding with polymers.



(a) bamboo powder



(b) pine powder

Fig.1 SEM micrographs of wood fibers (magnified by 300 times)

Two types of thermoplastic polymers are selected as the matrix material of WPC, one is polypropylene (PP, manufactured by CNOOC and Shell Petrochemical Co., Ltd), the other is copolyester hot-melt adhesives (Co-PES, manufactured by Shanghai TOMIS Materials Technology Co., Ltd) made by the polycondensation of butylglycol,

isophthalic acid and dimethyl terephthalate. Both simulation and experiments results demonstrate the SLS forming property of Co-PES is much better than that of PP (see section 4.2).

Two kinds of particle sizes of Co-PES are mixed respectively with dried wood powders using the high-speed mixer less than 40°C, one is about 60µm, the other is about 80µm. During the preparation of WPC, viscosity breaker, coupling agents and some other additives are joined into the composites evenly. Experiment results prove the mass ratio of wood powders should be less than 30% or it will be a problem for achieving desirable mechanical properties.

2.2. Laser Sintering of WPC

2.2.1 The preheating temperature of WPC

The setting of process parameters has the most crucial effect on the ability of material to be successfully processed by SLS[6]. The glass transition temperature (T_g) of WPC is gained by the analysis of its DSC curve, for predicting the feasible range of the preheating temperature. Amorphous polymer's optimal preheating temperature of SLS is empirically below the T_g 5~10°C to avoid agglomeration of the powder bed as well as to reduce the energy output of laser device.

DSC curves demonstrate the T_g of pine-WPC is approximately 85°C, the T_g of pine powder is about 100°C, and their composite's T_g is nearly 90°C seen as Fig.2. So, A desirable preheating temperature window of composite is set in [75°C,80°C].

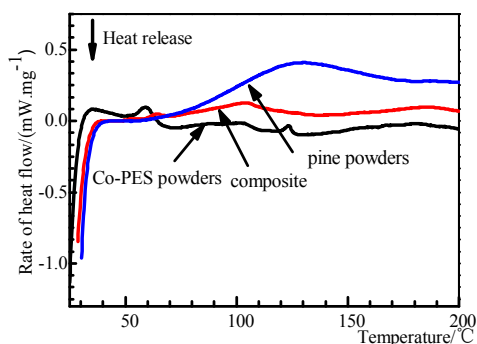
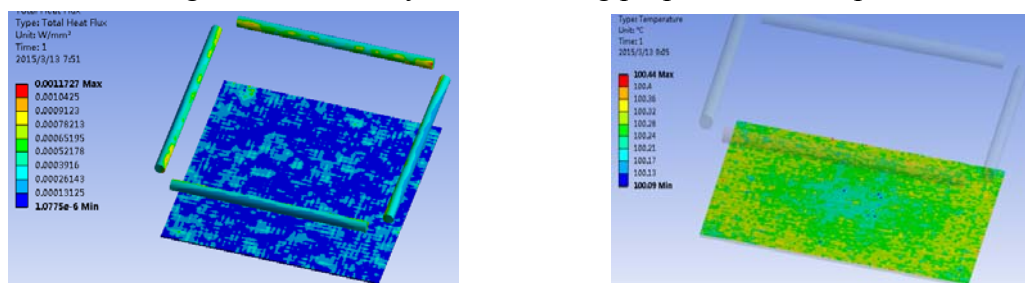


Fig.2 DSC curves of pine powders, Co-PES powders and their composites

The preheating temperature field simulation (Fig.3) about the HRPS-III A rapid prototyping machine built by ANSYS WORKBENCH illustrates there is an uneven temperature distribution on the powder bed when WPC is heated by infrared lamp heating system [7]. Fig.3 (b) tells the centre temperature is lower than those of outer areas thus causing an inconsistency in the forming properties of SLS parts.



(a) Cloud picture of heat flux on powder bed (b) Cloud picture of temperature distribution

Fig.3 ANSYS simulation for WPC preheating temperature field

2.2.2 SLS device and process parameters

The sintered WPC parts are manufactured successfully by both HRPS-III A rapid prototyping machine from Wuhan Lakeside Science & Technology and AFS360 rapid prototyping device fabricated by Longyuan AFS Co., Ltd. The process system of HRPS-III A rapid prototyping machine is shown as Fig.4, a CO₂ laser source is used with a wavelength of 10.6μm, its maximum output power is 55w, and the diameter of laser beam is 0.4mm.

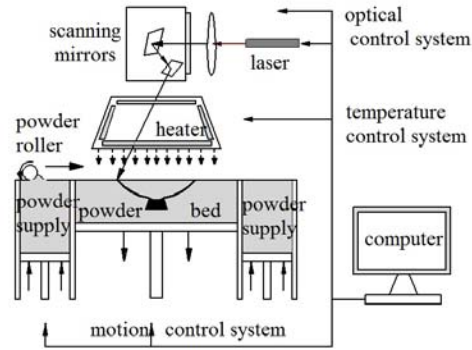


Fig.4 Schematic of HRPS-III A rapid prototyping machine process system

Experiment results indicate the proper laser power for WPC to be sintered is lower than those for the common SLS materials, which ranges from 7~14W depending on different types of wood powders and mass ratios of main raw materials. For example, when the mass ratio of wood powder and Co-PES is 1:4, the feasible laser powers of pine-WPC, bamboo-WPC, cellulose-WPC are respectively 7~10W, 8~11W, 11~14W. The rest process parameters of SLS of WPC are basically in common: the scanning speed is between 1800mm/s to 2200mm/s, the scanning space is from 0.1mm to 0.2mm, whilst the layer thickness is set between 0.1mm~0.2mm.

Laser sintering mechanism of WPC

3.1 Forming mechanism of sintered WPC parts

Three-dimensional finite element models of a single-line laser beam working on a layer of WPC powder bed are set up by the simulation software called ABAQUS based on the energy behavior of Gaussian distribution [8] (shown as equation (1)). The model is used for evaluating temperature fields of laser sintering under different laser powers (Fig.5) [9].

$$I(x, y, \omega) = I_0 \exp\left(\frac{-2(x^2 + y^2)}{\omega^2}\right) \quad (1)$$

Where I_0 is the maximum laser energy, ω is characteristic radius of laser spot, (x, y) is the coordinates relative to the center of laser spot.

Results from simulation and SEM micrographs show WPC will absorb most of the energy from CO₂ laser beam and transform it into heat. Segmental motion of Co-PES powder is activated rapidly as the temperature is above T_g , and Co-PES powders bond together or spread over the wood fiber as soon as gathering enough thermodynamic

free energy to drive physical changes (see Fig.6). The short period of sintering process can be divided into three stages: 1) Co-PES particles contact and sintering necks are shaped, 2) sintering necks grow, 3) channels of pores become closed and porosity is reduced. So physical change illustrates viscous flow is the main forming mechanism of SLS with WPC material.

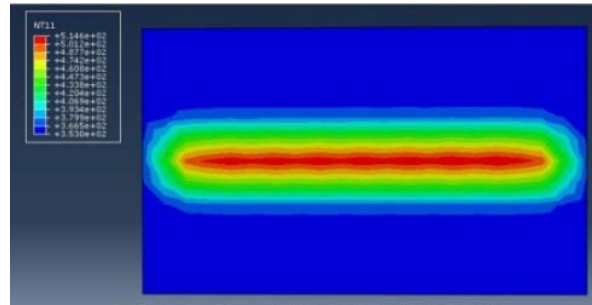


Fig.5 Distribution of temperature field on WPC powder bed surface (air natural convection coefficient is $13\text{W}/(\text{m}^2 \cdot ^\circ\text{C})$, effective emissivity of the powder bed is 0.85, the diameter of laser spot is 0.4 mm, preheating temperature is 80°C , the scanning speed is 2000 mm/s, layer thickness is 0.1mm, laser power is 10W)

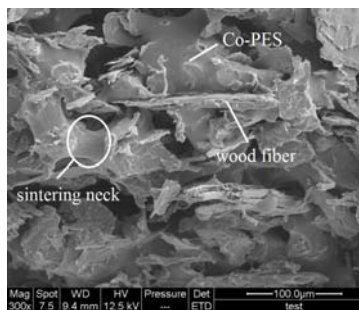


Fig.6 Fracture morphology of sintered pine-WPC parts (magnified by 300)

3.2 Interfacial bonding mechanism of sintered WPC parts

Interfacial bonding is a vital consideration for composites in SLS process because of its effects on mechanical and forming properties. FTIR result of pine-WPC before and after SLS shows there is no new chemical functional groups appearing, which means the interfacial bonding between pine powder and Co-PES doesn't include chemical bonding. It is the same result for eucalyptus-WPC, hence the change of the materials during sintering can be considered as physical changes [10]. The rough surface of wood fiber is conducive to mechanical interlock with Co-PES.

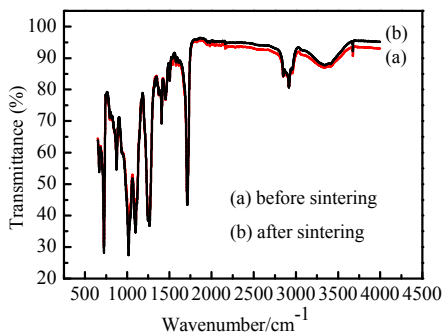


Fig.7 FTIR curves of WPC before and after sintering

Molecular dynamics simulation of sintering WPC

4.1 Build molecular models of WPC

Molecular dynamics simulation (MD) is applied to assist the study on SLS process of microcrystalline cellulose-WPC on a micro level and also to reduce labor intension. It is need firstly to build macromolecular chains of microcrystalline cellulose, PP, and Co-PES, considering the rationality of models and workload of computer, polymerization degree of the three molecular chains are chosen 20. Molecular models of cellulose/Co-PES blends and cellulose/PP blends in different mass ratios are set up through Amorphous Cell module on the conditions of 16°C, 1.01×10^5 Pa after optimizing the molecular chain structures.

4.2 The analysis of compatibility of WPC

The compatibility of cellulose powder respectively with PP and Co-PES is calculated via Blends Module of Materials Studio under their suitable preheating temperature. As can be seen from Fig.8 [11], the energy distribution curve of microcrystalline cellulose isn't coincident with any of PP or Co-PES. This phenomenon signifies microcrystalline cellulose is neither compatible with PP nor Co-PES, however, the different value of energy distributions of cellulose/Co-PES and Co-PES (shown as blue curve and green curve) is much lower compared to that of cellulose/PP and PP. Furthermore, it is verified experimentally WPC mixed by cellulose powder and PP powder fails to be processed by SLS, while WPC mixed by cellulose powder and Co-PES has a good processability as the SLS material.

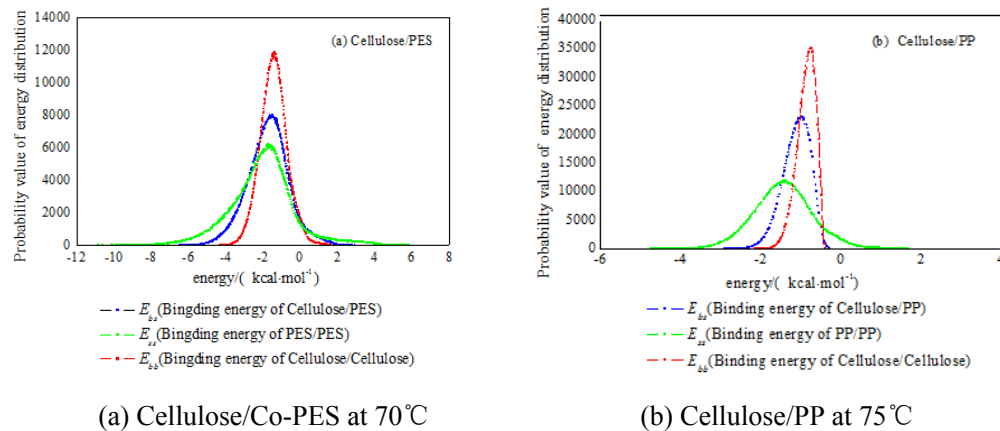


Fig.8 Binding energy distribution of composites of cellulose/Co-PES and cellulose/PP

4.3 Mass ratio optimization and simulation of cellulose-WPC

According to Flory-Huggins theory, miscibility of cellulose and Co-PES can be estimated by comparing its Flory-Huggins interaction parameter χ_{AB} with the critical value χ_C , the blend system is fully compatible if $\chi_{AB} \leq \chi_C$, otherwise it is not.

Five models of different mass ratios of blends are built to calculate their χ_{AB} in the system of MD. Fig.9 shows that χ_{AB} is closest to χ_C when the mass percent of cellulose is 25%, predicting the optimized mass ratio of cellulose and Co-PES is 25:75, and experiments results about the mechanical properties verify the prediction is right.

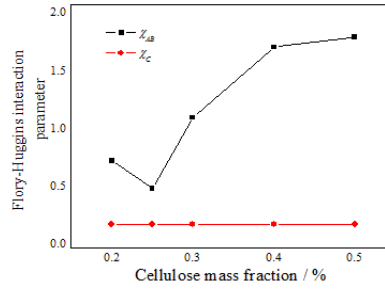


Fig.9 Flory-Huggins interaction parameter (χ) under different mass ratios

4.4 Simulation of the effects of temperature on the mechanical properties

Elasticity coefficient obtained on the basis of generalized Hooke law ($\sigma_i = C_{ij}\epsilon_j$, $i, j=1, \dots, 6$) is used for estimating plastic behavior and breaking strength. The mechanical properties under the condensed state of an amorphous material are isotropic due to its disordered molecular chain structure, so the elastic coefficient matrix $[C_{ij}]$ turns to be

$$[C_{ij}] = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{21} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{31} & C_{32} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$$

$$\text{and } C_{ij}=C_{ji}, \quad C_{11}=C_{22}=C_{33}, \quad C_{12}=C_{13}=C_{23}, \quad C_{44}=C_{55}=C_{66} = \frac{1}{2} (C_{11}-C_{12})$$

NVT ensemble and Forcite module are selected to calculate static elastic properties of cellulose/Co-PES blends under different temperatures in COMPASS force field, the results will do a favor to analyze the influence of temperature field on mechanical properties, shown in Table 1.

Table 1 Elastic property parameters of cellulose/Co-PES blends under different temperatures

Tempe- Rapture (°C)	Elasticity									Bulk modulus (K)	Shear modulus (G)	Tensile modulus (E)	Poisson's ratio(γ)
	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}				
40	13.35	10.13	9.60	2.26	2.91	2.40	7.05	7.23	5.77	7.38	2.39	7.98	0.32
50	14.53	12.27	11.73	2.98	3.40	3.28	7.35	7.74	7.05	8.58	2.85	9.27	0.32
60	14.67	12.42	11.93	3.13	3.76	3.36	7.70	8.68	7.15	9.12	3.56	9.85	0.32
70	14.75	12.51	11.95	3.47	3.79	3.40	7.79	8.73	7.17	9.27	3.62	9.90	0.32
80	15.25	12.56	11.98	3.63	3.89	3.41	7.87	8.84	7.23	9.28	3.63	9.97	0.32

Post-treating process and physical characterization of sintered WPC parts

5.1 Post-treating process of sintered WPC parts

Sintered WPC parts are porous, and the porosity of most sintered WPC parts is nearly 50%, except cellulose-WPC (the porosity varies from 28% to 31%), which is a negative factor for mechanical properties and anti-aging performance. Wax-infiltrated

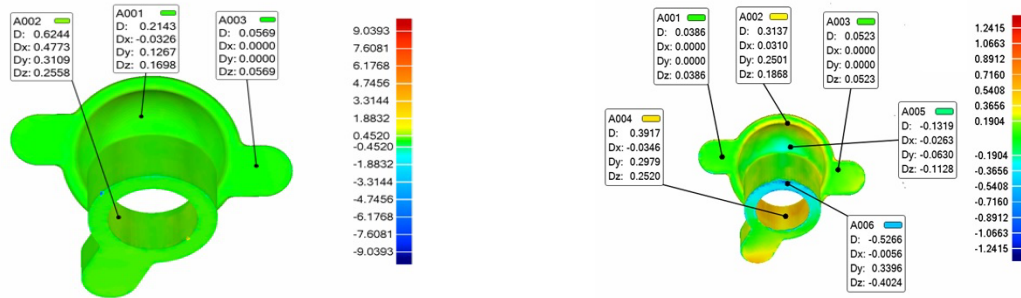
treating and epoxy resin-infiltrated treating are the two post-treating processes to improve the performance of sintered WPC parts.

Wax-infiltrated post-treating process is a relatively maneuverable approach to decrease porosity and strengthen mechanical properties. Before the process, putting the cleaned sintered WPC parts into thermostat at 60°C for preheating is an essential way to improve the degree of infiltration. During the process of infiltrating wax, the parts should be put into the melted wax (the temperature is kept around 75°C) slowly in case for uneven infiltration.

Since epoxy resin is viscous and this post-treating process is done at room temperature, the colloidal mixture containing epoxy resin and polyamide hardeners should be diluted by acetone solution or industrial alcohol to achieve a better viscous flow. The volume ratio of epoxy resin and polyamide hardeners is 1: (1~3), and the thinner's volume is one to two times of the sum volume of the other two reagents. As epoxy resin solution is hard to infiltrate into the porous WPC parts immediately, it is necessary to brush the parts with solution repeatedly as completely as possible to penetrate into the parts.

5.2 Quantity of sintered WPC parts

As a kind of amorphous material, WPC has higher viscosity than PA, which tends to forbid shrinkage and distortion, so high dimensional precision is easy for sintered WPC parts to achieve. Dimensional accuracy of sintered bamboo-WPC parts and their wax-infiltrated parts are tested through reverse engineering, and the average dimensional deviations of the green parts and wax-infiltrated parts are 0.29mm, 0.23mm.



(a) Sintered bamboo-WPC part (b) Wax-infiltrated sintered bamboo-WPC part

Fig.10 Three-dimensional deviations of sintered part and wax-infiltrated part

The surface roughness of sintered WPC parts, their wax-infiltrated parts, and the wax-infiltrated parts after polishing is tested by laser scanning confocal microscope. Ten different square areas (150μm×150μm) of each part are chosen randomly to measure the roughness values. It is certified the surface roughness of these three kinds of sintered WPC parts is separately less than 17μm, 13μm, and 5μm.

5.3 Mechanical properties of sintered WPC parts

Mechanical properties are vital concerns for SLS materials, which depend on many factors including the chemical and physical characteristics of the material itself such as particle size, surface tension and melt viscosity, the SLS machine linked to temperature field, process parameters, build orientation and placement, and also the post-treating processes.

To achieve better mechanical properties, the optimal mass ratio for a specific WPC is searched via experiments or MD, orthogonal experiment design and design of experiments (DOE) these two algorithms are applied to optimize component formula of WPC or process parameters. As for post-treating processes, the mechanical strength of sintered WPC parts after infiltrating epoxy resin is generally stronger than that after infiltrating wax. Moreover, Co-PES with particle size of 60 μm owns better surface quantity and mechanical properties than that of 80 μm when used as the matrix of WPC processed by SLS. Of all the WPC, cellulose-WPC has relatively better mechanical strength than others, however, its cost is higher than others. Here is the comparison about the previous mechanical strength of sintered WPC parts, current one, and the mechanical strength of sintered parts after wax-infiltrated post-treating and epoxy resin-infiltrated post-treating (as Table 2).

Table 2 The comparison of mechanical strength

	Past		Present		
	The green parts	Wax-infiltrated parts	The green parts	Wax-infiltrated parts	Epoxy resin-infiltrated parts
Tensile strength (MPa)	0.014~0.54	1.24~2.40	2.30~4.85	5.80~6.34	10.42~11.03
Bending strength (MPa)	0.22~0.48	0.76~2.73	8.22~10.69	10.43~11.70	15.13~19.02
Impact strength (KJ/m ²)	0.36~0.57	1.41~1.55	1.14~1.25	1.43~2.97	4.45~5.51

The application fields of laser sintered wood-plastic composites parts

6.1 Study on investment casting technology of sintered WPC parts

Investment casting is a promising industrial application field for manufacturing a complex-geometry component with high accuracy using a sintered WPC part as the fusible pattern. The wax-infiltrated SLS prototype made by eucalyptus/PES blends is assessed through thermo-gravimetric analysis before investment casting process. It is shown as Fig.11 the prototype's weight decreases dramatically when the temperature is between 290 $^{\circ}\text{C}$ and 490 $^{\circ}\text{C}$, the weight drops slowly and trends to stay stably when the temperature is above 490 $^{\circ}\text{C}$, and the weight of residuum is below 5% finally [12].

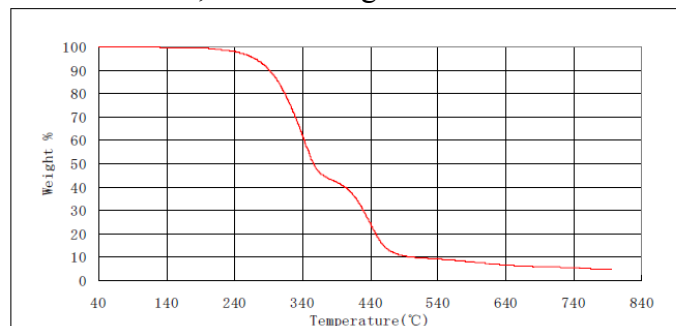


Fig.11 TG curve of wax-infiltrated prototype

The specific investment casting process is shown as Fig.12, the wax-infiltrated WPC part fabricated by SLS need firstly to be melt out by heating the assemblage in

stream at around 100 °C, then residual wood powder/Co-PES blends tend to burn out at a low temperature of 500~600 °C and a high-pressure air blast is used to blow out the ash. The mould still needs to be heated at high-temperature of approximately 1000 °C for oxidizing any residual residue before pouring the melted steel. A gear processed by investment casting combined with SLS technology is illustrated as Fig.13, and its surface roughness is 15µm before polishing.

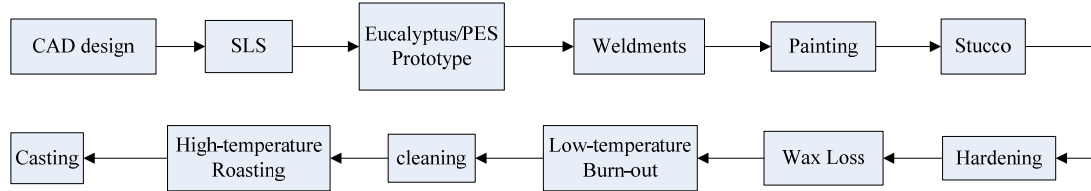


Fig.12 The investment casting process

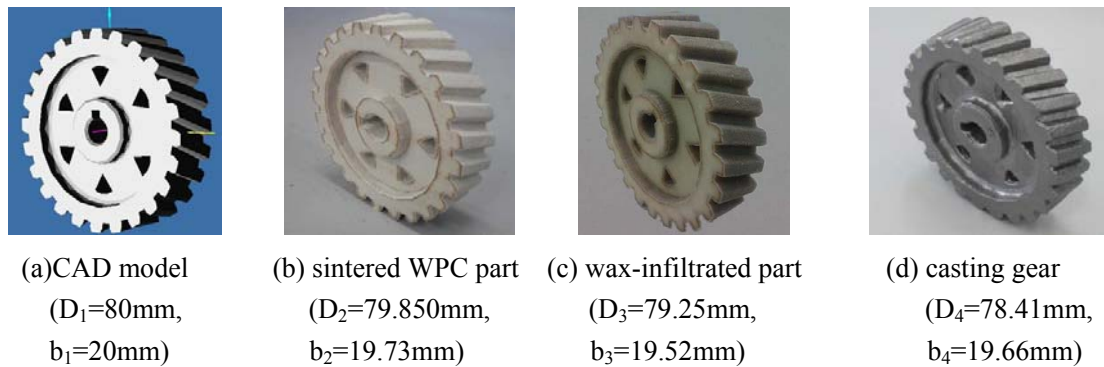


Fig.13 An example for investment casting of sintered WPC parts

6.2 Other applications of sintered WPC parts

The sintered WPC parts can not only be used for investment casting, but also can be applied in the fields of new product validation, exhibit fabrication, arts and so on with the advantages of high precision, low price and wood-like vision.

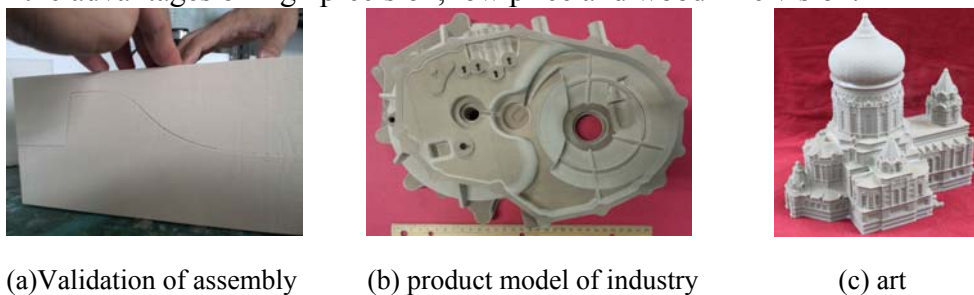


Fig.14 Examples for applications of sintered WPC parts

Conclusions

Diverse WPC used as a new promising kind of SLS material is studied in the past 14 years in order to provide a cheap and environmentally friendly material for SLS as well as to apply SLS in more application areas. The results prove WPC is ease of processing with a wide process window and smaller deformation than some polymers. The tensile strength, bending strength and impact strength of WPC without post-treating have been enhanced from 0.54MPa, 0.48MPa, 0.57MPa to 4.85MPa, 10.69MPa, 1.25KJ/m². What's more, the mechanical strength is respectively

improved to 6.34MPa, 11.70MPa, 2.97KJ/m² after infiltrating wax, 11.03MPa, 19.02MPa, 5.51 KJ/m² after infiltrating epoxy resin.

There is still much work to do for popularizing the application of SLS of WPC material, including fabricating more high mechanical strength sintered SLS parts, decreasing ash content for more high-precision investment casting.

Acknowledgements

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