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Improved green body strength using PMMA–Al_2O_3 composite particles fabricated via electrostatic assembly

Wai Kian Tan[1,*], Tatsuya Matsuzaki[2], Atsushi Yokoi[1], Go Kawamura[2], Atsunori Matsuda[2] and Hiroyuki Muto[1,2,*]

[1] Institute of Liberal Arts and Sciences, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan
[2] Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan
[*] Authors to whom any correspondence should be addressed.

E-mail: tan@las.tut.ac.jp **and** muto@ee.tut.ac.jp

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Abstract

In additive manufacturing, indirect laser sintering is used to process and fabricate ceramic materials using a polymer–ceramics green body. The mechanical strength of the green body is important to hold the shape and to enable the use of laser with low power density during the laser sintering process. Because the microstructure of the green body will considerably affect the density of the final product, this study demonstrated a feasible controlled formation of Poly (methylmethacrylate) (PMMA)–Al_2O_3 composite particles by an electrostatic assembly method that was used for the fabrication of the green body with improved mechanical properties, which were determine using an indentation test. The controllable homogeneous decoration of desired submicron-sized PMMA particles on Al_2O_3 particles allowed an effective use of PMMA additives while exhibiting considerable mechanical property improvement of the green body compared to poly(vinyl alcohol)-bonded Al_2O_3. The findings of this study show good potential of green body formation with improved strength for ceramics fabrication via indirect laser sintering.

1. Introduction

In the recent development of additive manufacturing, selective laser sintering (SLS) has been commonly used for customized ceramics manufacturing, which is difficult to achieve using conventional processing methods [1]. Although SLS is well-developed for polymers and metals, SLS of ceramics has experienced many challenges owing to the high melting temperature of ceramics [2]. The two types of SLS are direct and indirect laser sintering. The brittle nature of ceramics and high temperature gradient, which originates from the use of high power laser, have hindered the laser sintering fabrication of large ceramic components owing to delamination and cracking [3]. Therefore, indirect selective sintering, which involves the use of polymer–ceramic composites in the green body formation, allows the use of a lower laser intensity for the fabrication of a wide range of ceramic materials [4, 5]. Green body with homogeneous microstructure exhibiting adequate mechanical strength is vital for the subsequent process especially for complex and large components fabrication [6, 7]. Indirect laser sintering of ceramics such as alumina (Al_2O_3), is a process that involves the formation of a green body and binder removal, prior to sintering [3]. Various methods have been reportedly used for the green body formation that combine ceramic materials with a polymeric binder such as stereolithography [8], powder metallurgy [9], mechanical mixing [10], spray-dry [11], and core–shell ceramic–polymer composite powders by phase inversion technique [12]. Some studies have reported the use of polymer volume fraction as high as 50%, which led to large shrinkage and reduced strength. Therefore, it is essential to achieve an effective material usage for the green body fabrication without compromising its mechanical strength. Among the available polymer additives, poly (methyl methacrylate) (PMMA) is inexpensive and possesses a good amorphous polymer processing dimensional stability, which makes it a good additive candidate for application such as transparent functional fillers [13–15].

The objective of this study is to fabricate Al_2O_3 green body with improved mechanical strength using well-designed PMMA-Al_2O_3 composite powders. The design of the PMMA-Al_2O_3 composite powders was carried out using electrostatic assembly (EA) method in aqueous solution. The advantages of EA method include the controllability of additives decoration at nano- and micro-levels, applicability for materials with different shapes, cost-effective as well as good mixture homogeneity [16]. The feasibility of EA method for composite materials design for various applications have been reported recently, such as the formation of optical property controlled aerosol-deposited indium tin oxide (ITO)/cerium oxide-Al_2O_3 composite films [17], the formation of cellulose nanofiber decorated Al_2O_3 particles for selective laser sintering [18], the formation of carbon nanoparticles decorated Al_2O_3 granule composites with controlled mechanical properties [19], ITO or boron nitride decorated PMMA composites with controllable infrared filtering effect or heat conduction properties [13, 14] and fabrication of porous Al_2O_3–SiO_2 composite ceramics [20]. Besides that, this EA method is also used for materials development in energy-related field such as lithium-ion [21] and iron-air batteries [22]. Therefore, this study further demonstrates the possibility of using electrostatically- assembled polymer–ceramic composite particles for fabrication of green body with improved strength.

The PMMA–Al_2O_3 composites were obtained by EA method, where a relatively small volume fraction of PMMA particles (1 vol.% and 3 vol.%) was used to improve the strength of the final green body. In addition, the PMMA–Al_2O_3 composite powders could be used forgreen body formation via powder metallurgy method with potential application for indirect laser sintering of ceramics.

2. Experimental procedures

The experiments were carried out using commercially available PMMA (particle diameter: 400 nm, Soken Chemical Co. Ltd) and Al_2O_3 particles (average particle diameter of 3 μm from Sumitomo Chemical Co., Ltd). The polycation and polyanion used were polydiallyldimethyl ammoniumchloride (PDDA) (average molecular weight of 100,000–200,000, Sigma-Aldrich) and polysodium styrenesulfonate (PSS) (average molecular weight of 70,000, Sigma-Aldrich), respectively. Prior to electrostatic assembly, the surface charge of primary and secondary particles was modified using an electrostatic assembly, as reported in our previous work [23]. The surface charge of primary Al_2O_3 particles was made negative with the layer-by-layer assembly of PSS, PDDA, and PSS. For PMMA particles, the initial layer of sodium deoxycholate (SDC) was first coated onto its surface prior to PDDA to obtain a positively charged surface. Then, the suspensions were mixed and stirred to allow the electrostatic assembly process to occur. The composites that consisted of PMMA–Al_2O_3 particles with 1 vol.% and 3 vol.% ratios of PMMA were prepared. Then, the composite particle powders were obtained using the freeze-drying method. The green bodies were formed using the composite particle powders by uniaxial pressing at a pressure of 30 MPa followed by a heat-treatment at 200 °C for 30 min For comparison, green body, which consisted of only Al_2O_3, and Al_2O_3 particles with the addition of polyvinyl alcohol (PVA) (Wako Chemical Ltd) solution at 1 wt.% and 3 wt.% were also fabricated, pressed and heat-treated under the same condition. The PVA binder solution was added dropwise to the Al_2O_3 powders to obtain a wet mixture and hand-mixed using a ceramic mortar until a uniform mixture was obtained. The PVA-added Al_2O_3 composite powders were then dried overnight prior to pressing and heat-treatment. The morphological observation of the composite particles were carried out using a field emission electron microscope (FE-SEM, Hitachi S-4800). For the determination of mechanical properties, an indentation test was performed with a press-fitting speed of 0.03 mm min^{-1} and a maximum load of 1.5 N. A square pyramid diamond indenter (Vickers indenter: manufactured by Tokyo Diamond Tool Works) with an inclination angle of $\beta = 22°$ was used. For uniform evaluation, indentation was performed randomly at three spots for each sample.

3. Results and discussion

The SEM images of the starting materials, Al_2O_3 and PMMA particles used for this study are shown in figure 1. From the SEM images, it can be determined that the average diameter of Al_2O_3 and PMMA particles were 3 μm and 400 nm, respectively. Figure 2 shows the morphologies of composite particles obtained using 1 wt.% and 3 wt.% PVA-added Al_2O_3 particles as well as 1 vol.% and 3 vol.% PMMA-particles decorated Al_2O_3 particles. PVA was chosen for comparison because it is commonly and used as a binder in dry pressed ceramics [24]. In figures 2(a) and (b), the adherence of Al_2O_3 particles can be seen, and the interconnection between Al_2O_3 particles increased with a higher wt.% of PVA addition. Meanwhile, figures 2(c) and (d) show the morphologies of composite particles with the 1 vol.% and 3 vol.% addition of PMMA particles to 3-μm Al_2O_3 particles, respectively. It is observed that PMMA particles are homogeneously adsorbed onto the surface of Al_2O_3

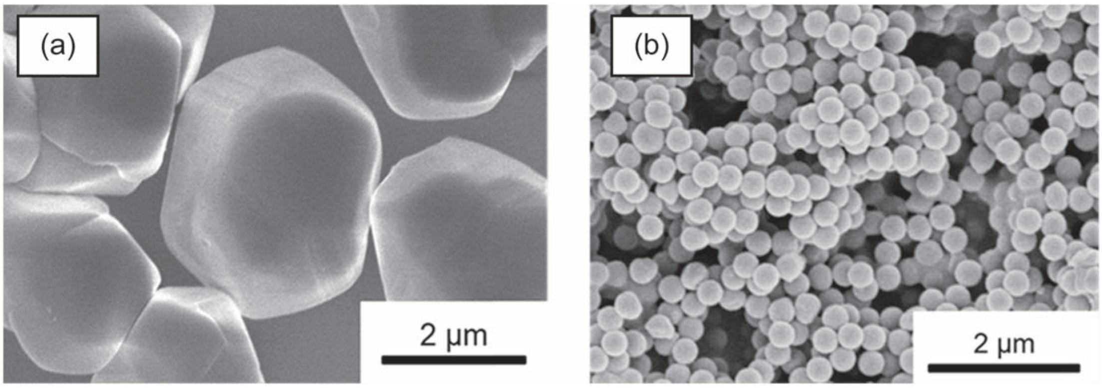

Figure 1. SEM images of the starting powder materials, (a) Al_2O_3 and (b) PMMA particles.

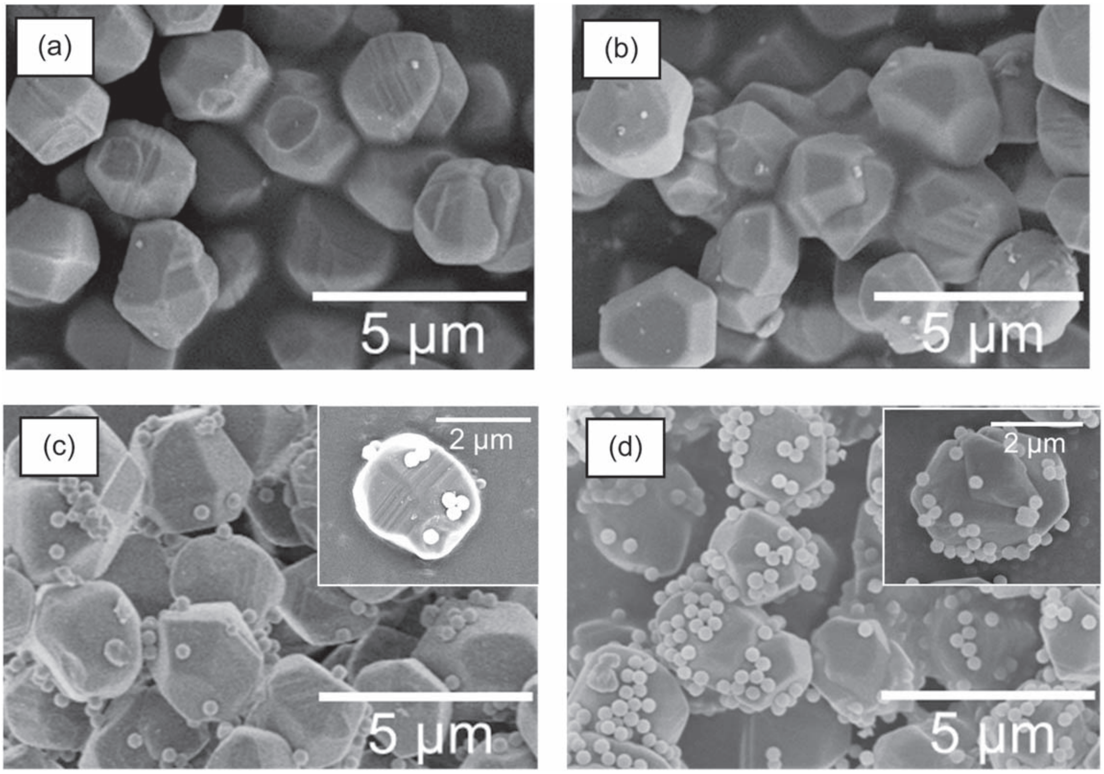

Figure 2. SEM images of the (a) 1 wt.% and (b) 3 wt.% PVA-added Al_2O_3 particles. The SEM images of PMMA–Al_2O_3 composite particles obtained using 1 vol.% and 3 vol.% PMMA addition via electrostatic assembly are shown in (c) and (d), respectively.

particles, as indicated by the insets in the respective images. The homogeneous distribution of PMMA particles within the Al_2O_3 powder forming the polymer–ceramic composites is essential for the formation of a strong green body [25]. From the SEM images, the amount of observed PMMA particles was clearly higher in the composite with 3 vol.% of added PMMA compared to those with 1 vol.% of added PMMA. This demonstrates the feasibility of electrostatic assembly in obtaining a controlled decoration of desired additive with good homogeneity [14, 23]. To form the green body, both the PVA-added Al_2O_3 composites and the PMMA–Al_2O_3 composites were pressed and heat-treated at 200 °C for 30 min. The morphological SEM images obtained are shown in figure 3. Figures 3(a) and (b) show the morphologies of the 1 wt.% and 3 wt.% PVA solution added Al_2O_3 particles while, figures 3(c) and (d) show the Al_2O_3 particles with 1 vol.% and 3 vol.% of PMMA particles added, respectively. As for the PVA-added Al_2O_3 composites, although no significant difference is observed, the adherence among the Al_2O_3 particles appears to be improved. On the other hand, as for the PMMA–Al_2O_3 composite particles, the formation of interconnected neck structures is clearly seen in both images (figures 3(c) and (d)). In the sample with 3-vol.% PMMA addition, in addition to necking structures, some remnant sheet-like PMMA was also observed owing to the incomplete melting of PMMA. For comparison purpose, the SEM

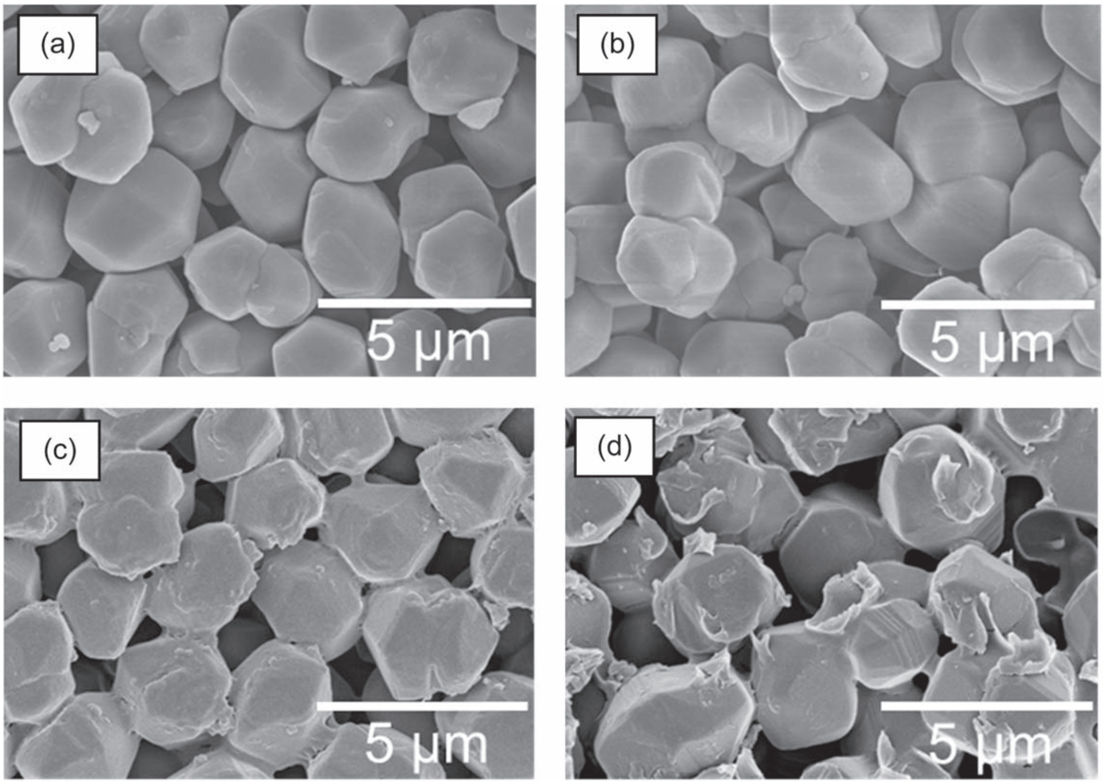

Figure 3. SEM images of the PVA-added Al_2O_3 composite particles obtained with (a) 1 wt.% and (b) 3 wt.% PVA binder solution as well as PMMA–Al_2O_3 composite particles obtained with (c) 1 vol.% and (d) 3 vol.% PMMA added after the heat-treatment at 200 °C for 30 min.

images of only pressed Al_2O_3 particles before and after heat-treatment at 200 °C for 30 min are shown in figures S1(a) and (b) (available online at stacks.iop.org/NANOX/1/030001/mmedia), respectively. By comparing the SEM images, no morphological difference is observed and the pellets formed were rather fragile and cracked into several pieces during handling. The mechanical property of the Al_2O_3 pellet after heat-treatment was first evaluated using indentation test and the result obtained is shown in figure S2. Figure S2 shows a *P–h* curve indicating the occurrence of a large press-fitting without reaching the maximum load of 1.5 N. This result indicated that the sample was very brittle with poor withholding strength when polymeric binder was not added. The mechanical properties obtained for the 1 wt.% and 3 wt.% PVA-added Al_2O_3 composites as well as the 1 vol.% and 3 vol.% PMMA–Al_2O_3 composites are shown in figure 4. Figures 4(a) and (b) show the *P–h* curves of the Al_2O_3 green bodies obtained using 1 wt.% and 3 wt.% PVA, respectively. For the green bodies fabricated using 1 wt.% PVA-added Al_2O_3 particles, the average maximum indentation displacement was approximately 55 μm, with a variable range of 50–60 μm. As for the green bodies obtained using 3 wt.% PVA-added Al_2O_3 particles, the average maximum indentation displacement decreased to approximately 43 μm, with a wider measurement range of 35–55 μm. These results indicate a low fraction of mechanical strength improvement when the amount of added PVA was increased from 1 wt.% to 3 wt.%. Besides that, the variation between three measurements conducted for the 3 wt.% PVA-added Al_2O_3 was larger compared to that of the 1 wt.% PVA added Al_2O_3 sample. This observation is resulted from the inhomogeneous distribution of PVA binder that occurred within the green body when a higher amount (wt.%) of PVA was added. It is also reported that the organic binder in PVA solution tend to migrate and segregate during drying process forming inhomogeneous polymer-rich region which subsequently affect the adhesion strength and uniformity [24, 26]. Regarding the mechanical strength of green bodies obtained using PMMA–Al_2O_3 composites, the *P–h* curves obtained using 1 vol.% and 3 vol.% PMMA–Al_2O_3 composites are shown in figures 4(c) and (d), respectively. During press-fitting, the maximum load of 1.5 N was achieved, and three measurement results were consistent compared to those of PVA-added samples. From the comparison of *P–h* curves, the maximum indentation displacement reduced from approximately 30 μm to 10 μm, for the green bodies obtained using 1 vol.% and 3 vol.% PMMA–Al_2O_3 composites, respectively. The indentation results showed a considerable improvement in mechanical properties and consistency owing to the good homogeneity of PMMA–Al_2O_3 composites [27, 28]. Similarly, these results indicate that mechanical strength of the PMMA–Al_2O_3 composite can be improved by changing the amount of added PMMA. From the *P–h* curves, the Meyer hardness for all four samples was

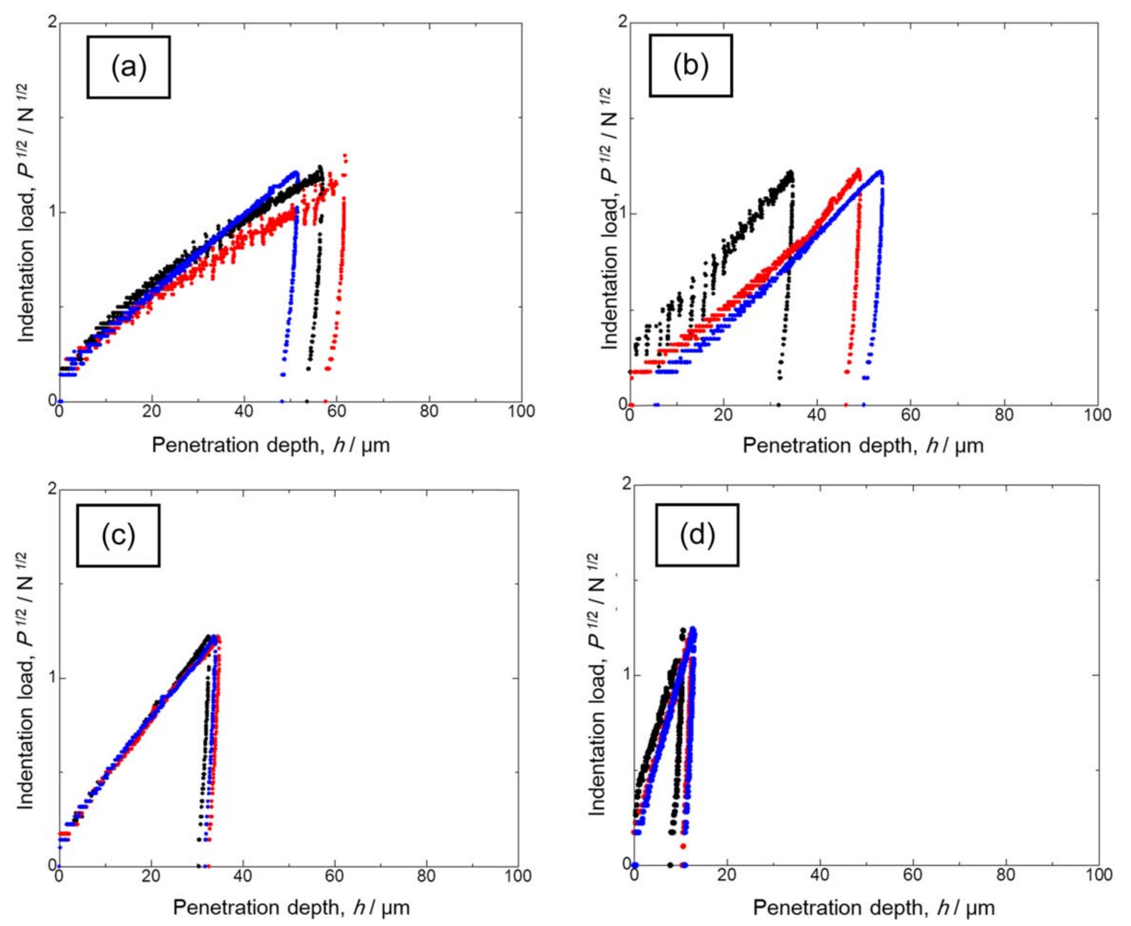

Figure 4. Indentation hysteresis of the green bodies obtained for (a) 1 wt.%, (b) 3 wt.% PVA-added Al_2O_3 particles, while (c) and (d) show the indentation hysteresis for 1 vol.% and 3 vol.% PMMA-added Al_2O_3 particles, respectively.

Table 1. Meyer hardness of the green bodies obtained using PVA- and PMMA-added Al_2O_3 composites.

	Meyer hardness [MPa]	
Amount of additive addition	PVA [wt.%]	PMMA particles [vol.%]
1	10	34
3	21	238

calculated and shown in table 1. The Meyer hardness for the 1 wt.% and 3 wt.% PVA-added samples was 10 MPa and 21 MPa, respectively. For the PMMA–Al_2O_3 composites, improved mechanical properties were obtained with the Meyer hardness of 34 MPa and 238 MPa for the sample with 1 vol.% and 3 vol.% PMMA addition, respectively. With a small incrementin the PMMA addition from 1 vol.% to 3 vol.%, the Meyer hardness increased by approximately seven times, indicating a considerable mechanical strength improvement of the compact green body. The results obtained from this study demonstrated the feasibility of a solid state green body formation using electrostatically assembled polymer–ceramic composite powders without using organic binder solution.

4. Conclusions

A feasible controlled design of composite particles that consisted of PMMA and Al_2O_3 particles was demonstrated using the EA method with the amount of added PMMA varied from 1 vol.% to 3 vol.%. Fabrication of green body was demonstrated using the PMMA–Al_2O_3 composite powders without using any organic binder solution. Good improvement in the mechanical property of the green bodies were obtained using

PMMA–Al_2O_3 composite powders compared to the PVA-added (binder solution) Al_2O_3. This was due to the improved homogeneity obtained from the uniform distribution of the PMMA particles on the surface of the Al_2O_3 particles. On the other hand, uneven coating and possible segregation of PVA binder in Al_2O_3 powdersresulted in a lower green body's strength. The results of this study show the possible formation of green body with improved mechanical strength using well-designed polymer–ceramic composite particles. Simple fabrication of green body with improved mechanical strength can be used for additive manufacturing such as indirect laser sintering.

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Declaration of competing interest

The authors have no conflict of interest to declare.

ORCID iDs

Wai Kian Tan https://orcid.org/0000-0002-0014-5475

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