Creation of polymer-ceramic materials for FDM printing

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Abstract. This paper discusses approaches and methods for obtaining highly filled polymer-ceramic materials to be used for additive manufacturing purposes. The key deliverable produced in the course of the project work was the development of polymer-ceramic materials that are suitable for extrusion processing and subsequent manufacture of products via Fused Deposition Modeling (FDM).

1. Introduction

Today, there is growing interest in new methods for obtaining three-dimensional microstructures which cannot possibly be produced using traditional techniques due to the exacting standards the resulting end products are expected to meet in terms of their geometry and accuracy characteristics. Three-dimensional ceramic microstructures are widely sought for use in modern devices, where the use of pure polymers would be impossible, such as in systems operating at high temperatures or in aggressive environments, as well as for the manufacture of products with increased tribological, mechanical, and chemical resistivity performance. Compared to almost all metals and polymers, ceramic materials can be used at much higher temperatures (over 1200 °C). Dense ceramics are characterized by high strength and hardness, while cellular ceramic structures are lightweight and highly resistant to thermal shock. While ceramics do outperform many other materials, they are often quite costly and laborious to produce. It is, thus, evident that the development of new approaches for producing ceramic materials making it possible to create three-dimensional ceramic products with a uniform surface and minimal post-processing requirements would be a step forward in the field of additive technology.

One side of how the desired characteristics can be achieved is by selecting and using a suitable ceramic filler, but what also plays an important role is the choice of the polymer binder, which is an essential component, not only for binding the particles of the ceramic filler, but also for extruding the polymer-ceramic precursor powder into filament, which is ultimately what makes it possible to build an end product using the FDM method.

Since the polymer binder is one of the main components of polymer-ceramic materials, it should be expected that the properties of the latter will be largely determined by the structure and composition of the polymers used. Organosilicon polymers can now be called a classic choice of inputs used for the production of polymer-ceramic materials. This is primarily due to their thermal stability, which is significantly superior to that of known organic polymers. Silicon-based polymers are capable of undergoing thermo-oxidative degradation while preserving the integrity of the main siloxane chain; this
process causes their lateral organic substituents to split off, after which the polymer molecules begin to sinter to those of the ceramic fillers, transforming the entire system into heat-resistant ceramics.

The choice of crosslinking agents can be made in favor of various low molecular weight organosilicon compounds containing functional groups, though some other reactive compounds may also be used for this purpose depending on the specific precursor performance characteristics required for a given ceramics product.

Yet another type of components that are important for building the polymer matrix of a binder are modifiers. Highly filled ‘binder – ceramic filler’ systems may show inadequate processing performance making it difficult to manufacture them into finished products. The significant viscosity and high flow point of such systems make them difficult to process by extrusion or molding. The addition of modifiers helps not only to simplify the processing of the ceramic precursor, improving the mixture system characteristics such as viscosity, flow behavior, and plasticization rate as well as reducing the curing time and temperature for the polymer binder, but also to improve the operating performance of the finished product.

The traditional method for reducing the viscosity and improving the flow behavior of filled systems is by loading the system with various plasticizers that penetrate into the polymer’s intermolecular space and weaken the interaction between the polymer molecules, changing their spatial arrangement. Even a small amount of plasticizer is enough to reduce the viscosity of the filled system. On the seamy side, however, plasticizer loading often leads to deterioration in the physical and mechanical characteristics of the material.

An alternative method used to reduce viscosity is to incorporate surfactants into the system. The large weight content of ceramic particles in the system turns it into a paste, where the binder quantity is not sufficient to uniformly wet all the particles and create polymer interlayers between them. In such systems, surfactant loading makes it possible to add more filler without increasing the viscosity of the system. However, a surfactant, when added to a ceramic precursor, will, much like a plasticizer, lead to a sharp deterioration in the strength of the resulting material, since it will form extra adsorption layers on the surface of the filler particles, thereby reducing the number of polymer-filler contacts.

The process of transforming a polymer-ceramic precursor into an end product via FDM imposes additional requirements on the properties of the system being developed. While FDM is, indeed, the easiest way one can imagine for tackling additive manufacturing when dealing with polymeric materials, there have been practically no accounts in the literature to date of any printing jobs being accomplished with the use of pre-ceramic polymers, which is apparently due to the rigidity and brittleness that characterize both polymer binders and systems filled with ceramic fillers. For this reason, any attempts to transform the binder-filler mixture into a polymeric filament having a uniform thickness and capable of being used in FDM printing have generally failed. It was proposed in [1] that, to obtain a stable flexible filament suitable for use in 3D printing, a silicon-based polymer be mixed with a thermoplastic polymer, which would provide the system with sufficient flexibility during filament extrusion and printing. It was shown in [1] that the thermoplastics used for this purpose will have completely decomposed in the course of the curing of the polymeric organosilicon binder and during the subsequent annealing process and will, thus, not affect the properties of the product. The end-product porosity will be determined by the binder/thermoplastic/filler ratio and will decrease in proportion to the decrease in the mixture’s thermoplastic content.

A workable polymeric formula to be used as a binder in next-generation highly filled polymer-ceramic materials for additive manufacturing will, consequently, include a high-temperature polymeric (mainly using organosilicon oligomers or polymers) binder, which may then be mixed with a thermoplastic polymer and/or modified with various additives that will improve the performance of the resultant polymer-ceramic mixture and facilitate its processing.
2. Result and discussion
The following siloxane polymer matrices and modifiers as well as the following filler content variations were used in the experimentation activities focusing on the production of polymer-ceramic materials in powder form:

- OMS;
- OMCTS;
- VTMOEO;
- TDEDC;
- Al₂O₃ (micro/nano: 50/50) 40 to 80 % wt;
- SiC (micro/nano: 50/50) 40 to 80 % wt;
- BN (micro/nano: 50/50) 40 to 80 % wt;
- ZrO₂ (micro/nano: 50/50) 40 to 80 % wt;

Details of the materials are set forth in Table 1.

### Table 1. Characteristics of input materials.

| No. | Full name                      | Abbreviated name | Molecular structure schematic | Role in the material                                    |
|-----|--------------------------------|------------------|-----------------------------|---------------------------------------------------------|
| 1   | Oligomethylsiloxane            | OMS              | *\(\text{Si} - \text{O} \)\_n\* | Polymer matrix (binder)                                 |
| 2   | Octamethylcyclotetrasiloxane   | OMCTS            |                             | Modifier (catalyst that improves the crosslinking process during firing) |
| 3   | Polydimethylsiloxane           | PDMS             | *\(\text{Si} - \text{O} \)\_n\* | Polymer matrix (binder)                                 |
| 4   | Polyethylene vinyl acetate      | PEVA             |                             | Polymer matrix (binder, thermoplastic polymer to reduce filament fragility) |
| 5   | Vinyltris-(2-methoxyethoxy) silane | VTMOEO         |                             | Modifier (crosslinking agent)                          |
| 6   | Tin diethyl dicaprylate        | TDEDC            |                             | Modifier (catalyst for crosslinking and curing)        |
| 7   | Aluminum oxide                 | Al₂O₃            | Al₂O₃                       | Ceramic filler                                         |
| 8   | Silicon carbide                | SiC              | SiC                         | Ceramic filler                                         |
| 9   | Boron nitride                  | BN               | BN                          | Ceramic filler                                         |
The polymer matrix and the modifier (see Table 2 for the ratio) were mixed with toluene in quantities needed to obtain 100 g of a 70-percent solution (70 g of the polymers and modifiers and 30 g (35 ml) of toluene); the solution was prepared in a glass with a capacity of 1000 ml via mechanical stirring. The mechanical stirrer was then replaced by a mechanical disperser, the solution was loaded with weighed portions of the filler and the ceramic filler (their weights being calculated based on the desired content levels). The reaction mass was dispersed at 20,000 rpm for 60 minutes. When the mixing process was finished, the reaction mass was poured into Petri dishes and dried in air overnight. Next, it was transferred to a vacuum oven and dried to constant weight at 100 °C / 5 mm Hg. The output was a polymer-ceramic material in powder form with colors varying from white to gray, depending on the type of polymer matrix and ceramic filler used.

As evident from Table 2 data, the technique developed for the purposes hereof is suitable for different polymer matrices with different filler loadings and is capable of producing dispersions that remain stable for a long time.

Table 2. Validating the technique for producing polymer-ceramic materials in powder form.

| No. | Mass fractions of components (%) | Dispersion stability over 8 hours |
|-----|---------------------------------|---------------------------------|
|     | OMS | OMCTS | VTMOEO | TDEDC | Al₂O₃ | SiC | BN | ZrO₂ |
| 1   | 52.6 | 5.26 | 1.42 | 0.72 | 40 | - | - | - | + |
| 2   | 52.6 | 5.26 | 1.42 | 0.72 | - | 40 | - | - | + |
| 3   | 52.6 | 5.26 | 1.42 | 0.72 | - | - | 40 | - | + |
| 4   | 52.6 | 5.26 | 1.42 | 0.72 | - | - | - | 40 | + |
| 5   | 43.8 | 4.38 | 1.18 | 0.59 | 50 | - | - | - | + |
| 6   | 43.8 | 4.38 | 1.18 | 0.59 | - | 50 | - | - | + |
| 7   | 43.8 | 4.38 | 1.18 | 0.59 | - | - | 50 | - | + |
| 8   | 43.8 | 4.38 | 1.18 | 0.59 | - | - | - | 50 | + |
| 9   | 21.9 | 2.19 | 0.59 | 0.29 | 75 | - | - | - | + |
| 10  | 21.9 | 2.19 | 0.59 | 0.29 | - | 75 | - | - | + |
| 11  | 21.9 | 2.19 | 0.59 | 0.29 | - | - | 75 | - | + |
| 12  | 21.9 | 2.19 | 0.59 | 0.29 | - | - | - | 75 | + |
| 13  | 17.5 | 1.75 | 0.47 | 0.23 | 80 | - | - | - | + |
| 14  | 17.5 | 1.75 | 0.47 | 0.23 | - | 80 | - | - | + |
| 15  | 17.5 | 1.75 | 0.47 | 0.23 | - | - | 80 | - | + |
| 16  | 17.5 | 1.75 | 0.47 | 0.23 | - | - | - | 80 | + |

The polymer-ceramic materials produced as shown above were subjected to relevant analytical tests to determine if they could possibly be processed into 3D printing filaments via methods such as injection molding and extrusion. The polymer-ceramic materials were studied to determine their respective melt viscosities and glass-transition temperatures. The data obtained are set forth in Table 3.

Table 3. Research test results.

| Sample | Melt viscosity, Pa·s | Glass-transition temperature, °C |
|--------|---------------------|-------------------------------|
| OMS/OMCTS/VTMOEO/TDEDC /40 Al₂O₃ | 9.0 | 140 |
| Sample                                      | Melt viscosity, Pa·s | Glass-transition temperature, °C |
|---------------------------------------------|----------------------|---------------------------------|
| OMS/OMCTS/VTMOEO/TDEDC /40 SiC              | 9.2                  | 132                             |
| OMS/OMCTS/VTMOEO/TDEDC/40 BN               | 9.3                  | 133                             |
| OMS/OMCTS/VTMOEO/TDEDC/40 ZrO₂             | 8.6                  | 134                             |
| OMS/OMCTS/VTMOEO/TDEDC/50 Al₂O₃            | 8.8                  | 134                             |
| OMS/OMCTS/VTMOEO/TDEDC/50 SiC              | 8.5                  | 135                             |
| OMS/OMCTS/VTMOEO/TDEDC/50 BN               | 9.3                  | 148                             |
| OMS/OMCTS/VTMOEO/TDEDC/50 ZrO₂             | 9.3                  | 149                             |
| OMS/OMCTS/VTMOEO/TDEDC/75 Al₂O₃            | 9.1                  | 147                             |
| OMS/OMCTS/VTMOEO/TDEDC/75 SiC              | 9.2                  | 140                             |
| OMS/OMCTS/VTMOEO/TDEDC/75 BN               | 9.1                  | 141                             |
| OMS/OMCTS/VTMOEO/TDEDC/75 ZrO₂             | 9.0                  | 143                             |
| OMS/OMCTS/VTMOEO/TDEDC/80 Al₂O₃            | 9.2                  | 142                             |
| OMS/OMCTS/VTMOEO/TDEDC/80 SiC              | 9.2                  | 143                             |
| OMS/OMCTS/VTMOEO/TDEDC/80 BN               | 8.9                  | 142                             |
| OMS/OMCTS/VTMOEO/TDEDC/80 ZrO₂             | 9.1                  | 147                             |

3. Conclusion

We have, thus, harnessed new approaches for obtaining next-generation highly filled polymer-ceramic materials to be used for additive manufacturing purposes.

The material choices we have made to produce polymer-ceramic materials that could be processed into 3D printing filaments via intensified methods such as injection molding and extrusion included systems of highly filled organic polymers combined with organosilicon ones (olydimethylsiloxane and polyethylene vinyl acetate) as well as systems of organosilicon polymers (oligomethylsiloxane) only. The required system viscosity decreases and flow behavior improvements were achieved by loading the filled polymers with plasticizers, surfactants, and low molecular weight modifier additives (octamethylcyclotetrasiloxane, vinyltris(2-methoxyethoxy)silane, diethyltin dicaprylate), which were also involved in forming the polymer’s cross-linked structure.

The project’s overall aim of developing polymer-ceramic materials that are suitable for extrusion processing and subsequent manufacture of products via FDM may, therefore, be considered accomplished.

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References

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