Investigation of polymer materials properties to use for additive manufacturing

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Abstract. The paper focuses on properties of polymers to produce core–shell ceramic powders (Al₂O₃, TiC, ZrO₂–Y₂O₃, TiB₂, SiO₂, SiC, ZrB₂, Si₃N₄, TiN, B₄C) and to set selective laser sintering (SLS) parameters to make ceramic prototypes with complex shape and bionic design. Polymer materials: polyvinyl alcohol (PVOH) grades V, 8/1, 16/1; polyvinyl acetate (PVAc) grades M10 and M100; polyamide (PA) grades 12 carbon, 6/66/610 – 1, 6/66 – 4, 54/10 (6/66 – 1), polystyrene (PS) grades 525M and 825M were investigated to determine glass transition temperature (T_g), melting (T_m) and crystallization (T_c) points, as well as thermal effects in nitrogen, argon and air. Polymers were heated to temperature comparable to the melting point with step of 5 °C/min and were cooled to 20 °C with differential scanning calorimeter (DSC).

1. Introduction

Ceramic powders are rarely used for additive manufacturing (selective laser melting or selective beam electron melting techniques etc.) due to its extremely high melting points comparison to widely applied powders of steels and alloys.

The most famous additive manufacturing methods are fused deposition melting (FDM) and selective laser sintering (SLS). FDM is based on the solid – to – fluid transition of thermoplastic filaments, passing through heated nozzle to predetermined place with further cooling and solidifying. SLS method consists of two stages: first stage is formation of thin continuous layer; second stage is using laser irradiation to bind powder particles in X and Y planes [1 – 4].

To accelerate the ceramic production with minimal shrinkage after printing, it is needed to develop new methods to produce core – shell ceramic materials (core – ceramic particle, shell – polymer). Polymer plays important role during selective laser sintering because it binds ceramic particles each other.

There are not so many commercially available polymers that can be used in additive manufacturing. So, to expand the material base, Lehmann & Voss & Co KG proposed to use composite material that includes at least one thermoplastic polymer and dispersed inorganic filler. As a thermoplastic polymer, it uses polyether ketone (PEK), polyetherether ketone (PEEK), polyphenylene sulfide (PPS), polyamidimide (PAI), polysulfonone (PSU), polyether sulfone (PES), polyphenyl sulfone (PPSU) and mixtures thereof. Researchers [5–6] noted that polydimethylsiloxane (PDMS) can be chosen as a thermoplastic polymer for a composite material. In the further post–processing of finished parts for all proposed polymers, rather toxic, corrosive solvents are used.

The aim of this work is evaluate the melting temperature (T_m) and glass transition temperature (T_g) for commercially available polymers to refine printing parameters for further selective laser sintering (SLS) of core – shell ceramic powders to get ceramic precursor with complex shape and bionic design.
2. Experimental

The measurements were carried out on NETZSCH DSC 204 F1 Phoenix 1 differential scanning calorimeter in air or argon atmospheres and NETZSCH DSC 200 F3 Maya differential scanning calorimeter in nitrogen atmosphere. Temperature and sensitivity calibrations were carried out at normal pressure in the temperature range from 100 °C to 500 °C according to parameters of phase transitions of high – purity standards Hg, In, Sn, Zn, Bi, Pb, CsCl and C2H5COOH (99.99%) with heating rates 5 K/min. ASTM E967 – 08 (2014) and ASTM E968 – 02 (2014) standards were used for calibration. The sampling was carried out in dynamic atmosphere of nitrogen, argon, or air (gas flow 40 ml/min) with protective inert gas flow of 70 ml/min in aluminum crucibles in accordance with following temperature programs:

1. Heating from 20°C to \( T_{\text{max}} \), set for each polymer separately and indicated in table 1, heating rate = 5°C/min.
2. Cooling from \( T_{\text{max}} \) to 20 °C CR = 5 °C/min (refrigerant – nitrogen)

To fix glass transition temperatures while cooling and devitrification while heating (hereinafter referred to as \( T_g \), glass transition temperature) was carried out tests as specified with ISO 11357 – 2 (2013) and ASTM E1356 – 08 (2014) standards. A smoothed signal was used to determine the effects. Melting (\( T_m \)) and crystallization (\( T_c \)) temperatures were determined according to the E794 – 06 standard, which recommends giving for polymers not only the temperature of the beginning and end of the peak, respectively, for \( T_m \) and \( T_c \), but also other characteristics of the peak.

Table 1. Polymer materials and its melting points (theor.)

| No. | Short Name | Full Name | \( T_m \) (theor.) |
|-----|------------|-----------|-------------------|
| 1   | PVOH V     | Polyvinyl alcohol grade V | from 200°C |
| 2   | PVOH 8/1   | Polyvinyl alcohol grade 8/1 | from 200°C |
| 3   | PVOH 16/1  | Polyvinyl alcohol grade 16/1 | from 200°C |
| 4   | PVAc M10   | Polyvinyl acetate PVAc, M10 | from 120°C |
| 5   | PVAc M100  | Polyvinyl acetate PVAc, M100 | from 120°C |
| 6   | PA 12C     | Polyamide 12 carbon | 178 – 180°C |
| 7   | PA 6/66/610 – 1 | Polyamide 6/66/610 – 1 | 211 – 220°C |
| 8   | PA 6/66 – 4 | Polyamide 6/66 – 4 | 211 – 220°C |
| 9   | PA 54/10   | Polyamide 6/66 – 1 (54/10) | 211 – 220°C |
| 10  | PS 525M    | Polystyrene 525M | from 240°C |
| 11  | PS 825M    | Polystyrene 825M | from 240°C |

3. Results and discussion

Figures 1 – 22 show DSC curves in different atmospheres that are shifted relative to each other while maintaining the scale. Odd patterns correspond to heating, even ones – to cooling.

The first three samples are different grades of polyvinyl alcohol (PVOH), however, samples 2 and 3 are presumably more stable after melting in air than sample 1.

For sample 1, there is difference in the thermal effects after melting in air comparison to argon and nitrogen (the exothermic effect begins on heating, Figure 1, due to reduced \( T_{\text{max}} \)). The exothermic process, that is associated with oxidation, continues to be observed in the cooling segment (Fig. 2) until crystallization. DSC results correlate with visual observation in oven in air when melted PVOH begins to gradually darker. As for other effects, they are reproduced in all atmospheres: insignificant differences are observed only in the temperature range from 30 °C to 120 °C. It is most likely related to random spread during water evaporation from the sample after devitrification. The overlapping of the effects of evaporation and devitrification needs additional confirmation (measurement of weight loss with temperature).
For samples 2 and 3, similar difference is observed in the thermal effects after melting in air in comparison with argon and nitrogen (the exothermic effect begins upon heating, Figures 3 and 5). The exothermic process associates with oxidation, it is almost not observed in the cooling segment up to crystallization (Figures 4 and 6). Holding sample 2 in oven also caused weight loss and darkening. As for other effects, they are reproduced in all atmospheres.

According to [7, 8], the glass transition temperature is significantly affected with water content. Therefore, the cooling curves in this research for samples 1 – 3 can be considered more reliable than on heating (since after heating, water is removed from melt as much as possible). To determine the glass transition on heating, it was used thermal cycling or program with thermal modulation to separate the "reversible" signal – glass transition and the "irreversible" signal – evaporation, as, for example, in [8].

![Figure 1](image1.png)  
**Figure 1.** General view of the DSC curves of polymer 1 (PVOH V) upon heating 5 K/min in Ar, N2, and air

![Figure 2](image2.png)  
**Figure 2.** General view of the DSC curves of polymer 1 (PVOH V) upon cooling 5 K/min in Ar, N2, and air

![Figure 3](image3.png)  
**Figure 3.** General view of the DSC curves of polymer 2 (PVOH 8/1) upon heating 5 K/min in Ar, N2, and air

![Figure 4](image4.png)  
**Figure 4.** General view of the DSC curves of polymer 2 (PVOH 8/1) upon cooling 5 K/min in Ar, N2, and air

![Figure 5](image5.png)  
**Figure 5.** General view of the DSC curves of polymer 3 (PVOH 16/1) upon heating 5 K/min in Ar, N2, and air

![Figure 6](image6.png)  
**Figure 6.** General view of the DSC curves of polymer 3 (PVOH 16/1) upon cooling 5 K/min in Ar, N2, and air
Samples 4 and 5 were various grades of polyvinyl acetate (PVAc). Since PVAc presumably decomposed at 170 °C, the samples were not heated up above 155 – 160 °C. The PVAc samples had extremely low degree of crystallinity originally. After devitrification, cold crystallization starts in sample 4 (Figure 7), however, small amount of crystals is formed (the melting peak was either very small or absent), and after assumed melting point, decomposition began (endothermic effect after 120 °C in all atmospheres). Also released acetic acid oxidation is fixed in air (Figure 7, exo effect after 120 ° C). In sample 5 (Figure 9.), there was no significant cold crystallization and further melting slightly exceeded the baseline signal of heat capacity. It should be noted that sample 5 is more resistant to decomposition, which is possibly related to particle size of the samples. While cooling (Figure 8, 10), the DSC curves for samples 4, 5 turned out to be almost identical, and only glass transition effects were observed.

Samples 6 – 9 were different grades of polyamide (PA). Sample 6 have the highest crystallinity and narrowest molecular weight distribution of the sample series: it exhibits narrow melting peak. For this sample, there are practically no differences in all atmospheres (Figures 11, 12) – from 20 °C and up to the end of melting. The melt is resistant to oxidation (there are no exothermic effects, Figure 11). However, during cooling in nitrogen atmosphere in the temperature range from 40 to 60 °C, there is an artifact (Figure 12), which repeats the change in the temperature program (Appendix). Also, this sample most likely contains the least amount of water.

Also sample 7 stable in air, the thermal effects in three different atmospheres differed slightly from each other (Figure 13, 14). After devitrification, water evaporation begins, which overlaps the melting peak, because of peak is bifurcated and the beginning of melting peak cannot be determined. Both peaks are listed below, but it is unclear which of the two processes ends earlier.
Figure 11. General view of the DSC curves of polymer 6 (PA12C) upon heating 5 K/min in Ar, N\textsubscript{2}, and air

Figure 12. General view of the DSC curves of polymer 6 (PA12C) upon cooling 5 K/min in Ar, N\textsubscript{2}, and air

Figure 13. General view of the DSC curves of polymer 7 (PA 6/66/610 – 1) upon heating 5 K / min in Ar, N\textsubscript{2}, and air

Figure 14. General view of the DSC curves of polymer 7 (PA 6/66/610 – 1) upon cooling 5 K / min in Ar, N\textsubscript{2}, and air

For samples 8 (Figures 15 and 16) and 9 (Figures 17 and 18), there are some insignificant differences in the air atmosphere: they are practically absent during heating for sample 8, but upon cooling, the slope of the DSC curve differs for both samples: since in the absence of heat release – absorption signal is due to heat capacity, it is likely that after some time in air, polyamide is oxidized, and the oxidized product has a different heat capacity. For these samples, after glass transition, the evaporation process is also observed. Evaporation finishes before melting as well as it is obvious that small amount of water remains before melting (the peak may be bifurcated, or the onset of melting is significantly underestimated in comparison with dry polyamide).
Samples 10 and 11 were different polystyrene grades (PS). These samples are softened in the oven, but no melting effect is not detected, and therefore it can be assumed that the material provided belongs to atactic polystyrene. The difference in the shape of the glass transition effect from the S–shaped one upon heating (Figures 19 and 21) is most likely associated with changing in the adhesion of the samples to the bottom of the crucible during softening. There is no significant difference between the behavior of the samples in argon and nitrogen. But oxidation begins above 200 °C in air for sample 10 (Figure 20), and 180 °C – for sample 11 (Figure 22). The temperature, at which significant polymer oxidation begins, is related to kinetic characteristics and may change at different heating rates, different sample surface areas, etc. Sample 10 turns out to be significantly oxidized due to glass transition temperature decrease. The effect above 260 °C in inert atmosphere for sample 11 (Figure 21) is most likely associated with the onset of polystyrene depolymerization.
Table 2 (heating) and table 3 (cooling) show certain characteristic temperatures in nitrogen atmosphere ($N_2$).

For samples 4, 10, and 11, melting on heating and crystallization on cooling is not observed, for sample 5, crystallization on cooling, while during heating there is melting effect with a small area (the degree of crystallinity is very small, but nonzero).

Samples 6 and 9 turn out to be significantly crystallized by the time when the amorphous part can turn into glassy state: its amount turn out to be below the detection limit of the device.

Table 2. Melting and devitrification points when heated to 5 K / min in a nitrogen ($N_2$)

| No. | Short Name | $T_{\text{max}}$ | $T_g$(onset) | $T_g$(mid) | $T_g$(end) | $T_m$(onset) | $T_m$(peak) | $T_m$(end) |
|-----|------------|------------------|---------------|------------|------------|--------------|--------------|-------------|
| 1   | PVOH V     | 240              | Evap overlay, not possible in current mode (without thermal modulation) to separate the evaporation | 217        | 205        | 224          | 222          | 227         |
| 2   | PVOH 8/1   | 240              |               |            |            |              |              |             |
| 3   | PVOH 16/1  | 237              |               |            |            |              |              |             |
| 4   | PVAc M10   | 170              | 42            | 43         | 45         |              |              |             |
| 5   | PVAc M100  | 155              | 32            | 35         | 39         | N/A          | N/A          |             |
| 6   | PA 12C     | 210              | 39            | 46         | 55         | 175          | 181          | 183         |
| 7   | PA 6/66/610--1 | 230     | 50            | 56         | 60         | * N/A        | 154          | 165         |
| 8   | PA 6/66 -- 4 | 220     | 30            | 46         | 62         | 166          | 181          | 188         |
| 9   | PA 54/10   | 190              | 36            | 40         | 45         | 161          | 177*         | 184*        |
| 10  | PS 525M    | 250              | 89            | 92         | 96         |              |              |             |
| 11  | PS 825M    | 270              | 89            | 92         | 96         |              |              |             |

* Evaporation and melting processes overlap.

Table 3. Crystallization and glass transition temperatures upon cooling 5 K / min in nitrogen ($N_2$)

| No. | Short Name | $T_g$(onset) | $T_g$(mid) | $T_g$(end) | $T_m$(onset) | $T_m$(peak) | $T_m$(end) |
|-----|------------|--------------|------------|------------|--------------|--------------|-------------|
| 1   | PVOH V     | 60           | 63         | 86         | 193          | 200          | 200         |
| 2   | PVOH 8/1   | 58           | 70         | 84         | 173          | 179          | 179         |
| 3   | PVOH 16/1  | 65           | 72         | 81         | 185          | 192          | 192         |
| 4   | PVAc M10   | 34           | 40         | 44         |              | NO           |             |
| 5   | PVAc M100  | 33           | 40         | 46         |              | NO           |             |
| 6   | PA 12C     | NO           |            |            |              |              |             |
| 7   | PA 6/66/610--1 | 29     | 36         | 39         | 63           | 93           | 117         |
| 8   | PA 6/66 -- 4 | 32         | 44         | 53         | 123          | 132          | 143         |
| 9   | PA 54/10   | 30           | 41         | 45         | 134          | 141          | 150         |
| 10  | PS 525M    | 81           | 89         | 96         |              | NO           |             |
| 11  | PS 825M    | 81           | 90         | 98         |              | NO           |             |

Tables 4 (heating) and 5 (cooling) show certain characteristic temperatures in an argon atmosphere.

In general, there is coincidence of these values with the results in nitrogen atmosphere within the error limits for polymeric materials (± 1 °C for the middle glass transition temperature, the beginning and end of this interval are less stable characteristics; ± 1 °C for melting characteristics on heating, in
the case, if the sample is not very wet; and about 3–5 °C for crystallization on cooling, due to the stochastic nature of this process).

The glass transition temperature of wet polyamide is related to the water content and appears to be unevenly distributed across the samples. Mean glass transition temperatures differences up to 5 °C are more related to this random distribution than to the atmosphere.

### Table 4. Melting and devitrification points when heated to 5 K/min in argon (Ar)

| No. | Short Name | \( T_{\text{max}} \) | \( T_g(\text{onset}) \) | \( T_g(\text{mid}) \) | \( T_g(\text{end}) \) | \( T_m(\text{onset}) \) | \( T_m(\text{peak}) \) | \( T_m(\text{end}) \) |
|-----|------------|----------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| 1   | PVOH V     | 245                  | Evap overlay, not possible in current mode (without thermal modulation) to separate the evaporation | 217                    | 230                    | 233                    |                        |                        |
| 2   | PVOH 8/1   | 240                  |                        | 205                    | 222                    | 227                    |                        |                        |
| 3   | PVOH 16/1  | 240                  |                        | 210                    | 226                    | 230                    |                        |                        |
| 4   | PVAc M10   | 155                  | 26                     | 31                     | 37                     | N/A                    | 125                    | N/A                    |
| 5   | PVAc M100  | 155                  | 32                     | 36                     | 39                     | N/A                    | 118                    | N/A                    |
| 6   | PA 12C     | 200                  | 40                     | 46                     | 54                     | 174                    | 181                    | 183                    |
| 7   | PA 6/66/610–1 | 220                        | 52                     | 59                     | 63                     | * N/A                  | 157*                   | 165                    |
| 8   | PA 6/66–4  | 220                  | 28                     | 55                     | 82                     | 163                    | 179*                   | 187                    |
| 9   | PA 54/10   | 190                  | 38                     | 43                     | 48                     | 161                    | 169*                   | 187                    |
| 10  | PS 525M    | 265                  | 86                     | 91                     | 99                     | NO                     |                        |                        |
| 11  | PS 825M    | 200                  | 89                     | 92                     | 94                     | NO                     |                        |                        |

* Evaporation and melting processes overlap.

### Table 5. Crystallization and glass transition temperatures upon cooling 5 K/min in argon (Ar)

| No. | Short Name | \( T_g(\text{onset}) \) | \( T_g(\text{mid}) \) | \( T_g(\text{end}) \) | \( T_m(\text{onset}) \) | \( T_m(\text{peak}) \) | \( T_m(\text{end}) \) |
|-----|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| 1   | PVOH V     | 67                     | 72                     | 82                     | 193                    | 199                    | 207                    |
| 2   | PVOH 8/1   | 67                     | 70                     | 74                     | 167                    | 176                    | 186                    |
| 3   | PVOH 16/1  | 58                     | 72                     | 92                     | 185                    | 191                    | 197                    |
| 4   | PVAc M10   | 30                     | 36                     | 44                     | NO                     |                        |                        |
| 5   | PVAc M100  | 30                     | 36                     | 44                     | NO                     |                        |                        |
| 6   | PA 12C     | N/A                    | N/A                    | N/A                    | 153                    | 156                    | 158                    |
| 7   | PA 6/66/610–1 | 28                        | 35                     | 38                     | 73                     | 94                     | 132                    |
| 8   | PA 6/66–4  | 23                     | 43                     | 63                     | 124                    | 132                    | 142                    |
| 9   | PA 54/10   | 29                     | 40                     | 44                     | 134                    | 142                    | 150                    |
| 10  | PS 525M    | 86                     | 91                     | 99                     | NO                     |                        |                        |
| 11  | PS 825M    | 82                     | 89                     | 96                     | NO                     |                        |                        |

* Tables 6 (heating) and 7 (cooling) show certain characteristic temperatures in air.

Except for heavily oxidized samples (primarily 10), these values coincide with the results in nitrogen and argon atmosphere within the error limits for polymer materials (±1 °C for the middle glass transition temperature, the beginning and end of this interval are less stable characteristics; ±1 °C for melting characteristics on heating, in case the sample is not very wet; and about 3–5 °C for crystallization on cooling due to the stochastic nature of this process).

The glass transition temperature of wet polyamide is related to the water content and appears to be unevenly distributed across the samples. Mean glass transition temperatures differences up to 5 °C are more related to this random distribution than to the atmosphere.
Table 6. Melting and devitrification points when heated to 5 K / min in air

| No. | Short Name | $T_{\text{max}}$ | $T_g$ (onset) | $T_g$ (mid) | $T_g$ (end) | $T_m$ (onset) | $T_m$ (peak) | $T_m$ (end) |
|-----|------------|------------------|---------------|-------------|-------------|---------------|--------------|-------------|
| 1   | PVOH V     | 240              | 217           | 230         | 232         |               |              |             |
| 2   | PVOH 8/1   | 240              | 199           | 222         | 227         |               |              |             |
| 3   | PVOH 16/1  | 237              | 210           | 226         | 230         |               |              |             |
| 4   | PVAc M10   | 155              | 220           | 175         | 181         | 183           |              |             |
| 5   | PVAc M100  | 200              | 220           | 163         | 179         | 184           |              |             |
| 6   | PA 12C     | 230              | 190           | 175         | 183         | 187           |              |             |
| 7   | PA 6/66/610–1 | 220        | 190           | 175         | 178         | 184           |              |             |
| 8   | PA 6/66–4  | 220              | 200           | 175         | 184         | 190           |              |             |
| 9   | PS 525M    | 284              | 284           | 175         | 184         | 190           |              |             |
| 10  | PS 825M    | 200              | 200           | 175         | 184         | 190           |              |             |

* Evaporation and melting processes overlap.

Table 7. Crystallization and glass transition temperatures upon cooling 5 K / min in air.

| No. | Short Name | $T_g$ (onset) | $T_g$ (mid) | $T_g$ (end) | $T_m$ (onset) | $T_m$ (peak) | $T_m$ (end) |
|-----|------------|---------------|-------------|-------------|---------------|--------------|-------------|
| 1   | PVOH V     | 64            | 72          | 90          | 188           | 195          | 201         |
| 2   | PVOH 8/1   | 63            | 69          | 78          | 168           | 176          | 184         |
| 3   | PVOH 16/1  | 63            | 72          | 83          | 183           | 191          | 196         |
| 4   | PVAc M10   | 32            | 37          | 43          | NO            |              |             |
| 5   | PVAc M100  | 34            | 39          | 46          | NO            |              |             |
| 6   | PA 12C     | NO            | 28          | 39          | 57            | 92           | 121         |
| 7   | PA 6/66/610–1 | 28        | 36          | 39          | 57            | 92           | 121         |
| 8   | PA 6/66–4  | 23            | 39          | 47          | 124           | 132          | 142         |
| 9   | PA 54/10   | NO            | 23          | 39          | 47            | 124          | 132         |
| 10  | PS 525M    | 57*           | 76*         | 86*         | NO            |              |             |
| 11  | PS 825M    | 73            | 91          | 62          | NO            |              |             |

* The sample is highly oxidized, so the glass transition temperature is lower than in other atmospheres for sample 11, for which the program was stopped before burning.

4. Conclusions

The research shows accurate melting temperatures ($T_m$) and glass transition temperatures ($T_g$) in argon, nitrogen and air of different polymers (polyvinyl alcohol grades V, 8 / 1,16 / 1 ; polyvinyl acetate grades M10 and M100; polyamide grades PA12C, PA6 / 66 / 610–1, PA6 / 66–4, 54/10 (PA6 / 66–1), polystyrene grades 525M and 825M) to produce core–shell ceramic powders ($\text{Al}_2\text{O}_3$, TiC, $\text{ZrO}_2–\text{Y}_2\text{O}_3$, $\text{TiB}_2$, $\text{SiO}_2$, $\text{SiC}$, $\text{ZrB}_2$, $\text{Si}_3\text{N}_4$, $\text{TiN}$, $\text{B}_4\text{C}$) and set selective laser sintering (SLS) parameters to make ceramic prototypes with complex shape and bionic design.

It was revealed that the melting point of polymers differs from the theoretical one. PVOH V has melting temperature ($T_m$) 217 °C in air ($-9.58 \% T_m$ (theor.)); PVOH 8 / 1 – 199 °C in air ($-17 \% T_m$ (theor.)); PVOH 16 / 1 – 210 °C (in air) ($-11.39 \% Tm$ (theor.)); PVAc M10 – not set; PVAc M100 – 118 °C in air ($-41 \% T_m$ (theor.)); PA12C – 175° C (in air) ($-23.91 \% T_m$ (theor.)); PA6 / 66 / 610–1 –
155°C in air (- 29.54 % T_m (theor.)); PA6 / 66–4 – 163°C in air (- 25.90 % T_m (theor.)); PA 54/10 (PA6 / 66–1) – 161°C in air (- 15.26 % T_m (theor.)); PS 525M – not set; PS 825M – not set.

Glass transition temperatures (T_g) are indicated for next materials in air: PVOH V – from 64 °C to 90 °C; PVOH 8/1 – from 63 °C to 78 °C; PVOH 16/1 – from 63 °C to 83 °C; PVAc M10 – from 32 °C to 43 °C; PVAc M100 – from 34 °C to 46 °C; PA12C – not set; PA6 / 66 / 610–1 – from 28 °C to 39°C; PA6 / 66–4 – from 23 °C to 47 °C (in air); PA 54/10– not set; PS 525M – from 57 °C to 86 °C; 825M – from 73 °C to 91 °C.

Acknowledgment
The applied research efforts have been made possible with the state financial support received from the Ministry of Science and Higher Education of Russian Federation under Subsidy Grant Agreement No. 075–15–2019–1945 of December 20, 2019. (Unique Applied Research (Project) ID: RFMEFI60719X0327).

References
[1] Kotz F, Arnold K, Bauer W, Schild D, Keller N, Sachsenheimer K, and Rapp B E 2017 Nature 544 (7650) 337
[2] Eckel Z C, Zhou C, Martin J H, Jacobsen A J, Carter W B, Schaedler T A 2016 Science 351 (6268) 58
[3] Schmidt J, Colombo P. 2018 J. European Ceram. Soc. 38 57
[4] Zarek M, Layani M, Eliazar S, Mansour N, Cooperstein I, Shukrun E, and Magdassi S 2016 Virtual and Physical Prototyping 11 263
[5] Holger V and Rechberger M Composite material and its use in additive manufacturing methods 2017 U.S. Patent Application No. 16/622,436
[6] Lewis J A, et al. Printed three–dimensional (3D) functional part and method of making 2019 U.S. Patent No. 10,462,907. 29 Oct. 2019.
[7] Rault J, Gref R, Ping Z H, Nguyen Q T and Néel J 1995 Polymer 36 1655
[8] Konidari M V, Papadokostaki K G and Sanopoulou M 2011 J. Appl. Polymer Sci. 120 3381