The general approach to the 3D-printing process quality estimation on the modified polymer substrates

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Abstract. The parameters defined the items quality FDM 3D-printed on the flexible modified polymer substrates were determined as exemplified by monitoring the 3D-process of the periodical elements forming on the oxyfluorinated PELD and PET films aimed to the production of the prototype model of a lab-on-a-chip device. Due to SEM, EDS and FTIR techniques application the correlation between the modification mode parameters and the elements operating stability was connected. The general approach to the 3D-printing process quality estimation on the modified polymer substrates is shown.

1. Introduction

Both micro- and macro-structures targeted forming on the flexible surfaces is the one of the high-demand practical problems and fundamental one for various areas including flexible wearable and printed electronics [1–3], prototyping of different personal devices as well as microbiological or lab-on-a-chip devices [4–6]. Typically, traditional forming techniques of surface polymer structures (lithography, vacuum deposition, etc) are both multi-staged and expensive [7, 8]. Providing this fact, the actual research area is the demanded surface systems formation by 3D-printing using known but chemically modified both polymer and composite materials, including conductive one, aimed to the heterogeneous structure materials production [9–14].

Moreover, the problem of 3D-printing methodological support in terms of the process quality monitoring is unsolved due to complex interactions formation between the filament properties [15], the 3D-printer elements adjustment [16] as well as processing parameters combination (printing layer height, both extrusion and the supporting table temperature, printing velocity, the nozzle traverse speed, the items filled density, slicing procedure accuracy [17], etc.) at the production process (figure 1, left part of the figure).

It is evident that in case of the flexible substrates using, quality of the 3D-printed surface systems is above all listed others determined by the both morphology and properties of the polymer substrate and secondarily by the printing parameters finally resulted in the end filament-substrate adhesion value. Thus, one of the important monitoring stages of the 3D - elements (items) production is surface pre-treatment (modification) quality estimation.
In the study the monitoring parameters list of elements quality the FDM 3D-printed on oxyfluorinated PELD and PET films is offered based on the experimental verification of their validation.

2. Methods and materials

In the study such well-known parameters, but do not earlier used for the given purposes in terms of planar “on-substrate” 3D-printing quality estimation, as substrate surface morphology, wetting ability, composition, filament - substrate adhesion, were tested (figure 1).

![Figure 1](image)

**Figure 1.** Factors affected on traditional (bulk) 3D-printed items quality (lower part of the figure) and printed on the flexible polymer substrates.

Aimed to the pre-engagement stage performance monitoring of the 3D-printing on polymer substrate the two types test-object files (figure 2a, b) consisted of either parallel periodical lines with 1mm width (figure 2a) as the fluid channel prototypes or 1 sm² area disks with 1mm thickness (figure 2b) were created using Autodesk Fusion360; the slicing procedure was realized by Ultimaker Cura software.

The commercially available PELD (PKP Resurs Ltd., Russia) and PET (VHZ OJSC, Russia) polymer films were used as the test-object substrates and pre-processed according to the [10] at the various modification (oxyfluorination at the He-carrier gas atmosphere) conditions in order to the next 3D-printing parameters improvement:
Figure 2. The test-objects configuration: I – layout, II – photo of the 3D-printing process.

- the 1st processing mode (2 in figure 5) – in presence of fluorine (F) 10 wet.% and oxygen (O) 6 wet.%.
- the 2nd processing mode (3 in figure 5) – in presence of F 7.5 wet.% and O 10 wet.%
- the 3rd processing mode (4 in figure 5) – in presence of F 11 wet.% and O 4 wet.%

The both initial and modified substrates morphology factor was examined by FE-SEM analysis using Jeol JSM 7500F (1nm spatial resolution with 10-12nm Pt pre-coating). The chemical state of near-surface substrates layers was controlled by ATR-FTIR (FT-801, instrumented by ZnS crystal). The polymer surface properties (free surface energy ($\gamma_s$)) were defined by the contact angle measurements using fast video fixation procedure; the measurement results were processed by ImageJ software with DropSnake plugin; both the polar ($\gamma^p_s$) and dispersion ($\gamma^D_s$) energy components were calculated according to Van Krevelen’s formula.

The 3D printing of the test-objects was realized by Anycubic MegaS FDM-printer equipped the 200 $\mu$m brass nozzle diameter at the 210 °C and 30mm/sec velocity. The adhesion failure values were examined according to Russian State Standard 32299-2013 using the tensile testing machine PM-50. The 1.75mm PLA filaments (3D Systems, USA) were used for the test-objects production due to lower extrusion temperature as well as higher polar energy ($\gamma^p_s$) component in compare to ABS (table 1).

Table 1. The ABS and PLA parameter comparison.

| Material | Contact angle $\Theta$, grad | $\gamma^D_s$ mN/m | $\gamma^P_s$ mN/m | $\gamma_s$ mN/m |
|----------|------------------------------|-------------------|------------------|----------------|
| 1 ABS    | $79\pm8$ 54±4               | 21,7             | 9,1             | 30,8           |
| 2 PLA    | $66\pm8$ 48±4               | 12,1             | 24,0            | 36,1           |

3. Results

The well-known problem of the vast majority elements forming on the initial polymer surface is the low adhesion value which can be resulted in the item failure. It is also clearly visible in figure 3 (I) for the 3D-printed planar test-object (channels prototypes).

Despite both known subjectivity and quit poor accuracy, one of the wide spreading laboratory express analysis of the modification procedure quality is the surface properties monitoring by the contact angle measurement technique (table 2, figure 4). The technique allows to a priori predict the next technological substrate behaviour. So, we detected drastically reducing of substrate
contact angle resulted in the full wetting in case of PET substrate type using whereas surface energy of the PELD substrates is only doubled (table 2, figure 4).

The contact angle measurements accompanied with the calculated surface parameters $\gamma_s$, $\gamma_s^D$ and $\gamma_s$ (table 2) are well verified with filament – substrate adhesion analysis (figure 3) in case of the 3D-printed macro-disks testing. Indeed, the peel strength test of “filament – PET substrate” adhesion demonstrates about 20 times value increasing after the modification procedure (maximum, at the 180 min processing) - 1.2±0.1kPa for initial PET-PLA filament couple and 24.3±2.0kPa for oxyfluorinated PET-PLA one, respectively, with the quadratic dependency.

The fact affected on the filament – substrate adhesion parameter through the polymers surface properties changing is fluorine-containing (CHF, CF$_2$, CF$_3$) group formation as well as carboxy- or/and carbonyl-containing ones in the polymer chains that is detected by FTIR technique as it exemplified in figure 5 and table 3 (the fact correlates with [10]).

The FTIR-data were supported by the statistic significant EDS-results with the analysis depth factor accounting (figure 6). So, for the both PET and PELD substrates the maximum fluorine total amount is 7-8 wet% at the same modification mode.

However, the abovementioned results are not yet sufficient to allow definite conclusions for 3D “filament – substrate” adhesion management. In particular, the chemical composition of the near-surface layer can be variable due to environment action or/and aging. For example, additional carboxyl groups at the PET near-surface layer can be formed due to hydrolysis of the

**Table 2. PELD and PET surface parameters variation.**

| Substrate | Modification duration, min | Contact angle $\Theta$, grad $\theta_{water} \theta_{ethylenegl.}$ | Surface energy, mN/m $\gamma_s^D \gamma_s^P \gamma_s$ |
|-----------|-----------------------------|-------------------------------------------------|-------------------------------------------------|
| 1 PELD    | 0                           | 89±8 69±8                                      | 16.0±2.2 6.6±2.2 22.6±3 |
|           | 5                           | 56±4 28±2                                      | 17.4±2.2 27.3±2.2 44.7±3 |
|           | 180                         | 44±3 12±1                                      | 13.2±2.2 40.8±3 54.0±3 |
| 2 PET     | 0                           | 69±8 40±3                                      | 23.8±2.2 13.9±3 37.7±3 |
|           | 5                           | 10±2 13±2                                      | 1.3±0.5 87.7±2.2 89.0±4 |
|           | 180                         | 6±1 10±2                                      | 1.3±0.5 88.8±2.2 90.1±4 |
Figure 4. The fixation of the water drop creep-age on the oxyflourinated PET surface at the variation of the processing duration:
1 – 0 min;
2 – 1 min;
3 – 2 min;
4 – 5 min;
5 - 30 min;
6 - 60 min;
7 –180 min.

Figure 5. IR-spectrums of PELD (left) and PET (right) modified at various modes (in text above).

Table 3. The FTIR data of modified substrates for 3D-printing.

| Substrate | Structure fragments | Wavenumber, cm⁻¹ |
|-----------|--------------------|------------------|
| PELD      | C-F –C-H-F-(C=O)-C-H-F– and etc. | 1110-1000, 1730-1710 |
| PET       | C-F –C-H-F-C-(O)-O- and etc. | 1150-1130, 1820-1810 |

atmosphere water vapor after the modification procedure finishing, in contrast some part of the fluorine-contained groups can be evaporated from the layer. Due to this fact both FTIR and EDS analysis should be repeated.

Herein the not less significant factor for melted 3D filament-polymer coupling is the substrate morphology and not least because of roughness increasing. By SEM-analysis the last fact was tested: as it shown in figure 6 the modified surface is both more roughed and waved due to the macromolecules reordering. Moreover, in case of PET substrate the inverse-type surface structure transformation is detected. It is clear the less channels width, the higher morphology factor as well as defectiveness one. All listed monitoring factors aimed to the modification process managing allows to form the 3D-heterogeneous structures (channels) coupled with the
polymer flexible substrate.

Conclusion
The parameters, affected the “filament – substrate” adhesion as one of the quality parameters of the 3D-printed planar items, were defined. By SEM, EDS and FTIR techniques application the correlation between the polymer modification mode parameters and the 3D-elements operating stability was connected. The offered general approach to the 3D-printing process quality estimation on the modified polymer substrates was experimentally tested.

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