The effect of plasma treatment on the composition, structure and properties of filaments used in extrusion additive manufacturing

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The effect of plasma-chemical treatment on the surface properties of polylactide (PLA) and thermoplastic polyurethane (TPU) based filaments was studied. It is shown that the surface structuring contributes to a twofold increase in free surface energy of the polymer materials due to an increase in its polar component.

One of the main directions in chemistry and materials sciences research development is the creation of chemically and biologically resistant polymers [1-3] (in particular, using the techniques of additive prototyping and surface modification). The improved polymers are intended for sealing friction units in aviation, shipbuilding and mechanical engineering, to reduce the rate of biofouling of marine vessels, for medical and pharmacological purposes, and etc. There are several approaches to the formation of thin-film functional coatings (from the protective film attaching to the grafted monomers polymerization) [4]. Each of them is characterized by a certain resource and energy intensity, environmental friendliness, ergonomics and duration of treatment process, a special set of the protective coating physics-chemical characteristics (wettability, permeability, strength) and etc. In accordance with [5] it seems that the optimal combination of the factors is provided by the plasma-chemical surface modification technique. The descriptions of the original gas-phase and the plasma-chemical modification technologies (which have proven themselves well in providing chemical resistance and mechanical strength with respect to tangential shear deformations for a number of large tonnage polymers) is presented in [6]. In our study we've investigated the effect of plasma-chemical treatment on the surface properties of 3D-printed discs (manufactured with Anycubic Mega S 3D-printer at temperatures of 230 and 200^{o}C) made from PLA and TPU filaments often used in the extrusion additive prototyping.
It was shown in [8] that plasma-chemical treatment is most effective at a distance of 1.5-2 cm from the plasma source. At lower manifestations the thermal effect of plasma arc on the polymers surface turns out to be painful; at greater manifestations it is insufficient (there are no existing transformations on the surface of the experimental samples). The modification of 3D-printed discs by plasma-chemical treatment was carried out in accordance with the technique [7] by the open-type system APC-500 (Diener Electronic GmbH & Co. KG) (Figure 1) at a processing time of 60 seconds and a distance from plasma source to treating surface about 2 cm.
The modified 3D-printed discs did not have the damage in warping areas or surface cracks. The free surface energy γ_s (with polar γ_s^P and dispersive γ_s^D components) calculations was performed by the Owens–Wendt–Rabel–Kaelble (OVRK) method [10] (table 1). The required contact angles for distilled water Θ_w and ethylene glycol Θ_{eg} were measured using a KSVCAM 101 setup (KSV Instruments, Finland).

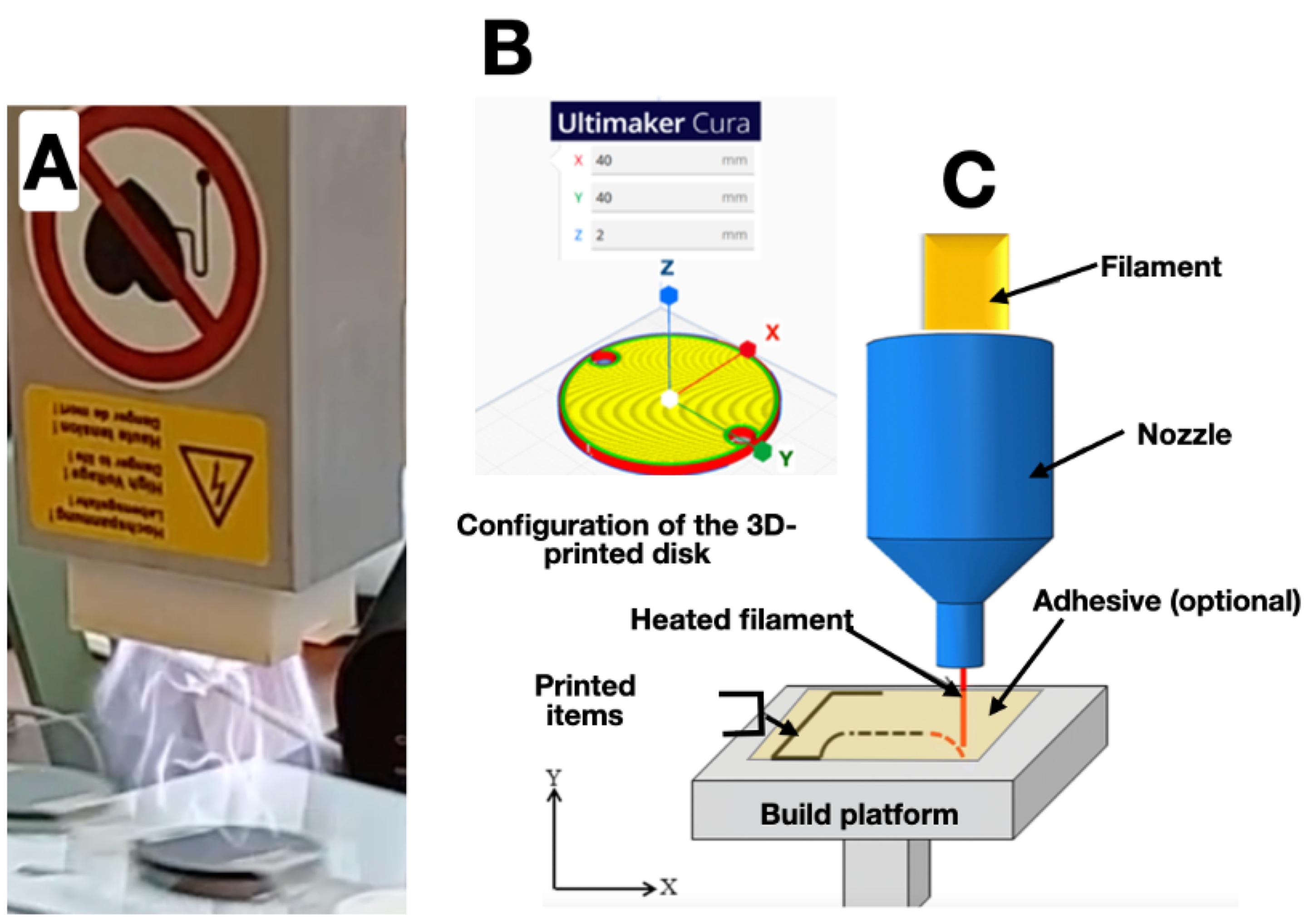

Figure 1 The plasma-chemical setup (A), the 3D-printed disk configuration (B), and the extrusion additive prototyping (FFF) flowchart (C)

Table 1 - Contact angle and surface energy values for original and modified 3D-printed discs

Polymer (manufacturer)		Contact wetting angle		γ_s, mJ/m^2	γ_s^D, mJ/m^2	γ_s^P, mJ/m^2
		Θ_w	Θ_{eg}			
TPU (FD Plast)	Ini.	74±2	56±2	30	13	17
	Mod.	42±2	39±2	64	3	61
PLA (CubeX)	Ini.	66±2	53±2	36	8	28
	Mod.	43±2	38±2	61	3	58

It has been established that the plasma-chemical treatment provides the possibility of direct hydrophilic-hydrophobic balance regulation for the surfaces of the considered 3D-printing materials (TPU and PLA filaments). It is due to the values of the polymeric materials free surface energy are doubled as the result of the carbonyl, carboxyl and other oxygen-containing groups formation in the polymers surface layers. This conclusion is confirmed by an increase in the polar component of the free surface energy (from 17 to 61 mJ/m^2 for TPU and from 28 to 58 mJ/m^2 for PLA).

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References

1. Bazaka K., Ostrikov K., Jacob M.V., Chrzanowski W, RSC Adv. 5 (2015) 48739.
2. Banerjee I., Pangule R.C., Kane R.S, Adv. Mater.. 23 (2011) 690.
3. Zhang X., Levänen E., Wang L, RSC Adv. 3 (2013) 12003.
4. Michelmore, A., Martinek, P., Sah, V., Short, R.D. and Vasilev, K., Plasma Processes Polym. 8 (2011) 367.
5. Laput, O., Vasenina, I., Salvadori, M.C., J. Mater. Sci. 54 (2019) 11726.
6. Назаров В.Г. Поверхностная модификация полимеров: монография / В.Г. Назаров. – М.: МГУП. 2008. – 474 с.
7. I. Dominguez-Lopez, M. Domínguez-Díaz, A.L. García-García, J.D.O. Barceinas-Sánchez, H. Martínez, , Mater. Lett. 285 (2021) 129159
8. Fahimeh Darvish, Navid Mostofi Sarkari, Mohammadreza Khani, Esmaeil Eslami, Babak Shokri, Mohsen Mohseni, Morteza Ebrahimi, Mahdi Alizadeh, Chang Fu Dee, Appl. Surf. Sci., 509 (2020). 144815
9. A. el moumen, Ahmed & Tarfaoui, Mostapha & Lafdi, Khalid. Int. J. Adv. Manuf. Technol. 104 (2019) 1.
10. Carina Waldner, Ulrich Hirn, Modeling, J Colloid Interface Sci. 640 (2023) 445.