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Analysis of the Solubility of a Support Filament Made of a Copolymer of Vinyl Alcohol and Butanediol in Aqueous Solutions with Variable pH

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ABSTRACT

3D printing is a modern technology that enables the creation of three-dimensional objects from various thermoplastic copolymers. One of the challenges of 3D printing is providing adequate support for complex shapes that may fall apart or deform during the printing process. Traditionally, support materials are used for this purpose, which are difficult to remove after printing and difficult to dispose of. This work focuses on the analysis of the solubility of the BVOH support filament in solutions with different pH values. In particular, the influence of pH on the dissolution time of the BVOH (Butenediol Vinyl Alcohol Co-polymer) copolymer in aqueous solutions and its influence on changes in the PETG base material from which the samples were printed were examined. It was found that the BVOH material combined with PETG is easily soluble in an alkaline environment.

Keywords: pH, 3D printers, FDM, BVOH, PETG, biodegradable materials, environmental protection.

INTRODUCTION

Fused Deposition Modeling (FDM) printing is a process of producing three-dimensional objects from a digital model [Szulżyk-Cieplak et al., 2014]. This process is carried out by applying layers of material on top of each other until the desired shape is obtained [Tomczyk Karolina et al., 2023]. Prototyping and manufacturing useful components using 3D printing has become a common phenomenon in recent years [Zaburko et al., 2021; Staniszewski et al., 2022]. Due to the variety of materials and low cost of devices, 3D printing technology is often used in industry, civil construction and various fields of science [Rahman, 2016; Ruśkowski, Gadomska-Gajadhur, 2017; Tay, Li, Tan, 2019; Paśnikowska-Łukaszuk et al., 2020]. This innovative approach not only reduces production costs but also has an impact on the natural environment [Cisneros-López et al., 2020; Amrita et al.2022; Paśnikowska-Łukaszuk et al., 2022]. Commonly used materials in 3D printing are thermoplastic polymer fibers that have been thermally processed and shaped into a filament [Malinowski, Łubkowski, 2012]. Some of them are synthesized until the end of production from artificial substances. The other most popular filaments are made from natural raw materials [Pinto et al., 2015; Wen et al., 2023]. These materials have many advantages, such as low price, ease of processing, friendliness to the environment and human health [Wen et al., 2023]. The OECD Global Plastics Outlook report shows that the amount of plastic waste will increase by 2060 [OECD, 2022]. It is therefore important to prepare appropriate technology and infrastructure enabling effective recycling of polymers of biological origin [Reddy, Raju, 2018; Amrita et al., 2022]. One of the materials that are increasingly used in 3D printing is PETG (polyethylene terephthalate glycol). The chemical bond is shown in Figure 1. It is a polyester copolymer based on terephthalic acid that has been modified with 50% ethylene glycol. This material combines the strength of ABS (acrylonitrile butadiene styrene) with the ease of printing PLA (polylactic acid). PETG is resistant to most chemicals such as acids, bases and solvents [Ambade et al., 2023]. It also has low processing shrinkage and good layer adhesion, but requires mechanical recycling [Latko-Durałek et al., 2019].

Support materials are used in 3D printing to provide support for parts of the elements that remain in space during printing. They are removed after printing, leaving the object intact. Among the biodegradable materials that can be used as a support material is BVOH copolymer (butenediol vinyl alcohol copolymer) [von Petersdorff-Campen et al., 2018; Jung et al., 2019; Ikebata et al., 2021; Yu et al., 2023; Xing et al., 2023]. It is a new, multifunctional and environmentally friendly material that combines formability and water-soluble biodegradability [Yu et al., 2023]. BVOH shows good hydrophilicity due to the large number of hydroxyl groups in its molecular chains. The molecular structure of BVOH influences its mechanical properties and corrosion resistance [Ikebata et al., 2021; Xing et al., 2023]. In addition, BVOH has good melt processability, which makes it easier to mix with other polymers. The chemical structure of BVOH is shown in Figure 2. This publication presents the results of research on the impact of pH on the solubility of BVOH as a support material and its impact on the physical properties of objects printed in 3D from PETG filament. The results of this research may be important for the further development of 3D printing and the protection of the natural environment.

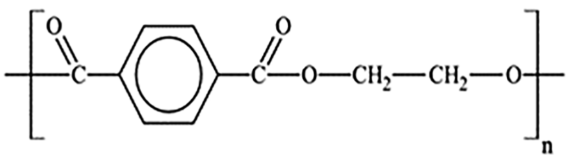

Fig. 1. Chemical structure of PETG copolymer

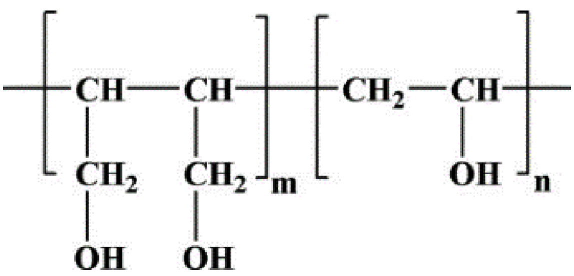

Fig. 2. Chemical structure of BVOH molecules

MATERIALS AND METHODS

The solubility of materials is the phenomenon of the decomposition of a solid into a liquid phase in order to obtain a homogeneous system [Grassi et al., 2011]. The aim of this work was to determine the influence of variable pH conditions on the dissolution time of the BVOH copolymer support filament. The base material consisted of PETG frames with dimensions of 60x60 mm and wall thickness of 5x5 mm. Sample models were prepared in the Autodesk Inventor 2023 engineering graphics program. This software is often used for spatial design and stress simulation using the finite element method [Hansen, 2013]. The sample model is shown in Figure 3. The sample model was saved to a file and using software dedicated to the printer, the code necessary to carry out the correct printing process was obtained (Figure 4). Earlier in the post-process, the samples were filled with BVOH support filament.

For printing, a printer was used that supports double extrusion technology for simultaneous printing with support and base filaments. Figure 5 shows the printed samples with visible supports inside. To test the solubility of the BVOH support filament, 6 solutions with a specific pH were prepared. The pH scale determines the quantitative scale of acidity and alkalinity of aqueous solutions of chemical compounds, defined as the negative logarithm of hydrogen ion activity (H^+) [Büker et al., 2021; Polidar et al., 2022]. The pH (Equation 1) defined as the negative logarithm of hydrogen ion activity (H^+).

$$pH = -\log[H^+] \tag{1}$$

Before immersion in the solutions, all samples were weighed and grouped, averaging the results. The weight of the samples is listed in Table 1. A series of solutions, each with a volume of 200 ml, were arranged. Containers 1 and 2 were filled with an acidic pH solution formed by hydrochloric acid (HCl). Container 3 held commercially obtainable alkaline water with a pH declared by the manufacturer. Containers 4 and 5 were filled with alkaline pH solutions obtained through the use of sodium hydroxide. The sixth container contained distilled water with a neutral pH level. Container 7 was

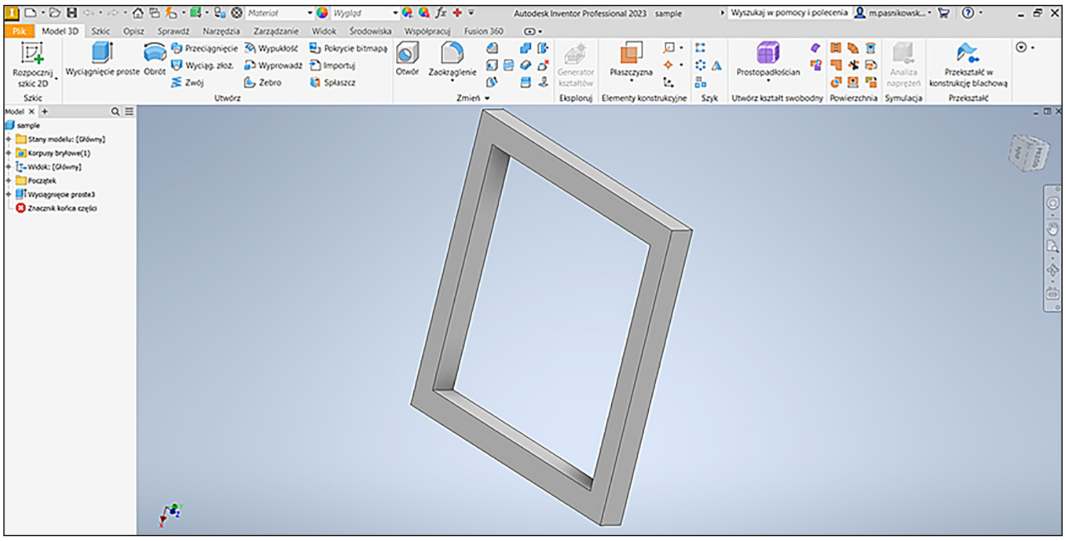

Fig. 3. 3D model of the sample in Autodesk Inventor

filled with an aqueous solution of unconfirmed pH and 12 g of a commercial activating powder that is intended for dissolving support filaments. This powder consists of anionic surfactants that accelerate the dissolution process. The pH and temperature of the solution were measured using the conductometric method at an ambient temperature of 25°C. The obtained pH values are listed in Table 2. To observe the changes occurring as a result of the reaction of the support material in the samples, the dissolution process was controlled using a camera with a time recording function. Comparisons of the change in sample mass were made at time intervals after 30, 60, 120, 180 min. The mass loss of the support filament was calculated using equation 2.

$$M_l = M_i - M_{it} \quad (2)$$

where: M_l – mass lost, M_i – initial specimen weight, M_{it} - specimen weight at time.

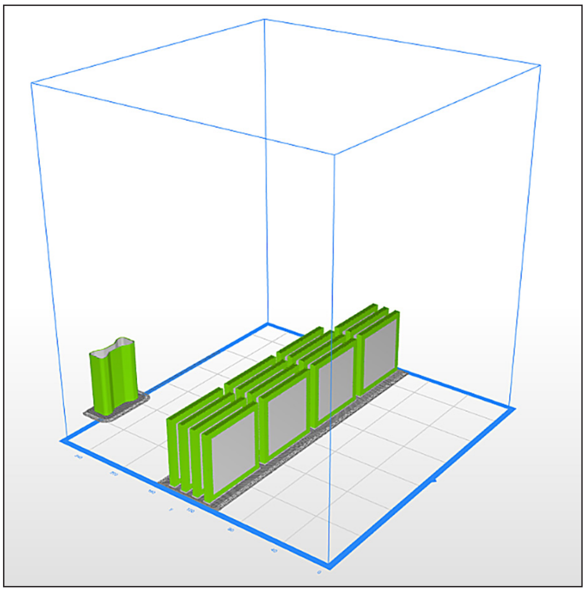

Fig. 4. Sample preview in slicer

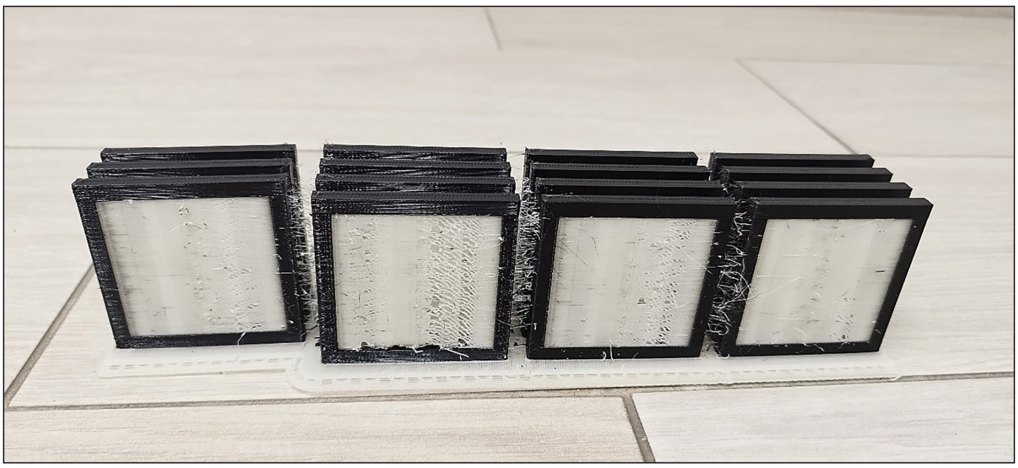

Fig. 5. 3D samples with stored supports

Table. 1 Average sample weights

Sample	1	2	3	4	5	6	7
Weight [g]	20.92	20.90	20.91	20.93	20.91	20.93	20.92

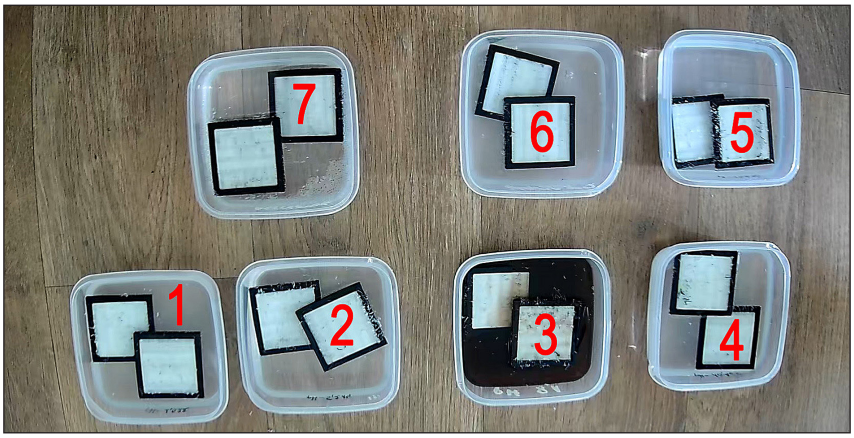

Fig. 6. The process of dissolving BVOH in aqueous solutions

Table 2. List of pH of solutions used

Solution	1	2	3	4	5	6	7
pH	1.522	5.214	8.1	10.765	13.265	7	Activator

RESULTS AND DISCUSSION

The aim of this experiment was to investigate the influence of variable pH conditions on the dissolution time of a filament made of a copolymer of vinyl alcohol and butanediol. These studies are important for understanding the influence of pH on the solubility and biodegradability of copolymer support materials. The summary of the obtained results is presented in Table 3. Preliminary research results indicate that the solubility of BVOH increases with increasing pH. Figure 7 shows the average results of BVOH mass reduction during dissolution at various pHs. The color of the points corresponds to the pH scale of the solution in which the samples were kept during the test.

The average time of complete dissolution of the support material in the tested samples is shown in Figure 8. In the prepared solutions with low pH, the BVOH material dissolved more slowly. This is related to changes in its molecular structure. The reaction of the low pH solution with BVOH produced micellar structures that are less soluble and disintegrated more slowly. In solutions with high pH, the reaction with BVOH creates branched structures that dissolve faster. In a solution with a pH of 13.265, the support filament was completely dissolved in the shortest time, but this resulted in the breaking of bonds in the structure of the base material. It was observed that the sample soaked in the solution with the highest pH became brittle. The effect of high pH is shown in Figure 9.

Table 3. BVOH weight loss over time

	pH indicator						
Time [min]	1	2	3	4	5	6	7
	1.522	5.214	7	8.1	10.765	13.265	Activator
30	0.12	0.24	0.48	0.54	0.72	0.98	0.08
60	0.48	0.96	1.92	2.28	3.32	3.84	0.34
120	0.96	1.92	4.56	3.84	5.76	7.68	1.56
180	1.92	2.88	5.76	6.84	8.64	11.52	3.2

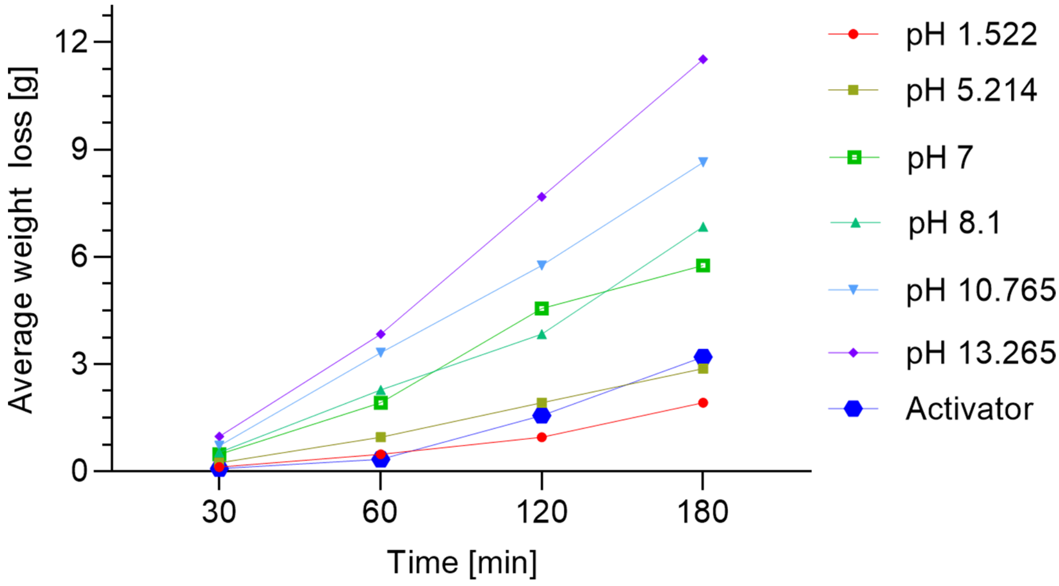

Fig. 7. Solubility of BVOH in various pHs at 25°C

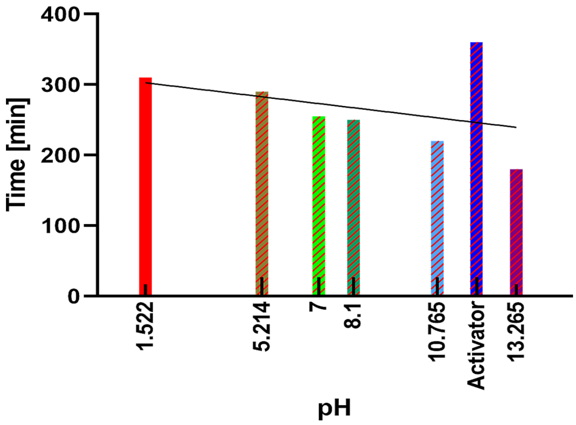

Fig. 8. Average dissolution time of BVOH in the tested samples

Fig. 9. Samples from the solution with the highest pH

In solutions between neutral pH 7 (distilled water) and alkaline pH 8.1 (alkaline water), slight differences in dissolution time were observed. Taking into account the availability of the product on the market, we can see that they can easily replace dedicated activators for dissolving the BVOH copolymer.

CONCLUSIONS

The research results presented in this paper showed that it is possible to test support filaments using aqueous solutions. BVOH, as a thermoplastic copolymer, is compatible with commonly available filaments, which means it can be used to print complex geometries and detailed elements. However, the more support structures there are in the model, the longer the dissolution process takes. Based on the test results, it is recommended to use solutions with an increased pH. These solutions are more effective at dissolving BVOH and the neutralization process is relatively simple. Additionally, it is recommended to use low-concentration solutions. Highly concentrated solutions may be hazardous to health and the environment. Therefore, you should avoid introducing them into the sewage system in large quantities, as it may disturb the biological balance. It is recommended to neutralize acidic or alkaline solutions before their disposal, and the choice of pH neutralization method should depend on the type of solution and its concentration.

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