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Research Article

Enhanced Solubility of the Support in an FDM-Based 3D Printed Structure Using Hydrogen Peroxide under Ultrasonication

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Fused deposition modeling (FDM), one of the archetypal 3D printing processes, typically requires support structures matched to printed model parts that principally have undercut or overhung features. Thus, the support removal is an essential postprocessing step after the FDM process. Here, we present an efficient and rapid method to remove the support part of an FDM-manufactured product using the phenomenon of oxidative degradation of hydrogen peroxide. This mechanism was significantly effective on polyvinyl alcohol (PVA), which has been widely used as a support material in the FDM process. Compared to water, hydrogen peroxide provided a two times faster dissolution rate of the PVA material. This could be increased another two times by applying ultrasonication to the solvent. In addition to the rapidness, we confirmed that amount of the support residues removed was enhanced, which was essentially caused by the surface roughness of the FDM-fabricated part. Furthermore, we demonstrated that there was no deterioration with respect to the mechanical properties or shape geometries of the obtained 3D printed parts. Taken together, these results are expected to help enhance the productivity of FDM by reducing the postprocessing time and to allow the removal of complicated and fine support structures, thereby improving the design capability of the FDM technique.

1. Introduction

For conventional manufacturing technologies, such as machining and molding processes, there has been enormous effort to improve their productivity by reducing lead times, costs, and material consumption. Recently, considering such manufacturing issues, the three-dimensional (3D) printing process has received much interest as an alternative. On the basis of its characteristic procedure of layer-by-layer integration, it enables the production of 3D freeform objects on the basis of digital CAD data while minimizing material consumption and maximizing the freedom of product design [1–5]. Moreover, as the trends in manufacturing technology have changed from mass production to mass customization in small batches, the applications of 3D printing techniques have exponentially increased in a variety of industries, including aerospace, automobile, medical device, construction, and electronics [6–8].

In ASTM F2792-12a [9], the types of 3D printing were separated into seven classes according to their process characteristics: binder jetting, direct energy deposition, material extrusion, material jetting, powder bed fusion, sheet lamination, and vat photopolymerization. Fused deposition modeling (FDM), which was originally invented in the infancy of 3D printing, is categorized into the group of material extrusion techniques that utilize a nozzle or orifice for selectively dispensing material. Owing to its various advantages, such as the low cost of the material/printer, simple working mechanism, and universality of material use, FDM has been

one of the most commonly and widely used systems not only in general industry but also among the research community.

A typical FDM process necessarily involves a set of build and support parts. The support structure has a role in preventing the overhung or undercut shape of the build structure from sagging or collapsing during the layer-by-layer printing process. As shown in Figure 1, there can be internal and external support structures depending on the structural morphology of the build structure. In the case of a single-nozzle FDM system, because both the support and build parts are printed by the same material, the support parts have to be stripped off manually, which unavoidably leaves some defective burrs on the surface of build part. Furthermore, in the manual process, it is not possible to perfectly remove the internal support parts that are embedded inside the build structure, including those in a void or cavity. To overcome these problems, dissolvable materials have been utilized as the support materials in dual-nozzle printing systems. Among the various dissolvable materials, polyvinyl alcohol (PVA) has attracted much attention as the support material owing to its water solubility, biocompatibility, mechanical flexibility, and low cost [10–13]. Even though PVA has shown suitability for serving as the FDM support part, there is still the limitation of the removal process with respect to dissolution time and possibility of residues. Especially for the hollow-shaped build structures such as the one in Figure 1(a), it essentially takes a considerable amount of time to remove the embedded internal support structure. To enhance the removal efficiency of PVA supports in a 3D printed part, several studies have attempted adjusting process parameters such as solvent temperature and applying agitation to improve solvent dissolution [14, 15].

Here, we introduce an efficient physicochemical method to promote the solubility of PVA support parts by using hydrogen peroxide (H_2O_2) and ultrasonication. The oxidative degradation effect of PVA in H_2O_2 has been investigated in the fields of textiles and pharmaceuticals and detergent- or adhesive-based industries [16, 17]. The main purpose of this study was to investigate the feasibility of H_2O_2 for removal of PVA supports in a 3D printed part. We first experimentally compared the solubility of PVA in water and H_2O_2 by applying each solvent to two different 3D printed parts: a PVA-only part and a build part with a PVA support. The superior dissolution rate in H_2O_2 was confirmed and was further enhanced by applying ultrasonication to the solvent. In addition to the fast dissolution rate, we investigate the residues of support material left on the build parts after the dissolution process. Additionally, by mechanical testing of H_2O_2-treated specimens and nontreated ones, we confirmed that there was no deterioration or degradation of build parts in terms of mechanical properties and shape geometries. Overall, we demonstrated the superior capability of a H_2O_2-based reagent in conjunction with ultrasonication with respect to efficiency of PVA support removal. These experimental results are expected to be useful for the postprocessing of 3D printed parts, particularly for a large number of support parts or difficult-to-remove parts with very complex shapes.

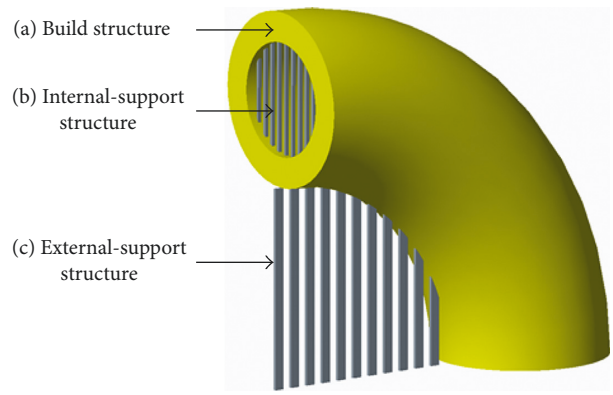

Figure 1: Schematic illustration of (a) build, (b) internal-support, and (c) external-support structures.

2. Materials and Methods

For the 3D printing of the build and support structures, two different thermoplastic filaments of polycarbonate (PC; Samyang Corp., South Korea) and polyvinyl alcohol (PVA; ESUN, China) were used, respectively. These filaments had a common standard diameter of 1.75 mm for an FDM-based 3D printer. The printing machine was a customized system equipped with two separate extruders that could separately dispense the build and support materials. For stable printing of materials, the temperature parameters of the PVA nozzle, PC nozzle, and chamber in the system could be set up to 220°C, 240°C, and 100°C, respectively. Under optimal conditions, prism shape samples of PVA-only and PVA/PC-combined parts were fabricated as representative structures with external and internal support parts, respectively.

For the dissolution process of printed parts, H_2O (distilled water) and H_2O_2 (30 wt% in H_2O, Sigma-Aldrich) were used and compared with each other in terms of dissolution rate. The printed parts were immersed into 500 ml of each solvent in a beaker that was loaded into a constant-temperature sonicator (TI-H10, Germany), which was set at a solvent temperature of 80°C and an applied frequency of 25 kHz. For analysis of PVA residues on the surface of build part, energy dispersive X-ray microanalysis (EDX, X-act, United Kingdom) was carried out using four types of 3D printed samples: one each of PVA and PC and two PC-PVA complex samples. The PVA and PC samples were prepared as reference controls. The two PC-PVA complex samples were prepared and dissolved in H_2O and H_2O_2 separately. To evaluate the change in mechanical properties after solvent treatment, the tensile test specimens were prepared according to the standard ASTM D638-1 and set onto a universal testing machine (EZ20, Instruments, United Kingdom). The tensile tests were performed at a rate of 5 mm/min.

3. Results and Discussion

3.1. Dual Printing of Build and Support Parts. Figure 2(a) shows our developed 3D printing system, which extrudes standard thermoplastic filaments in an FDM manner. It was

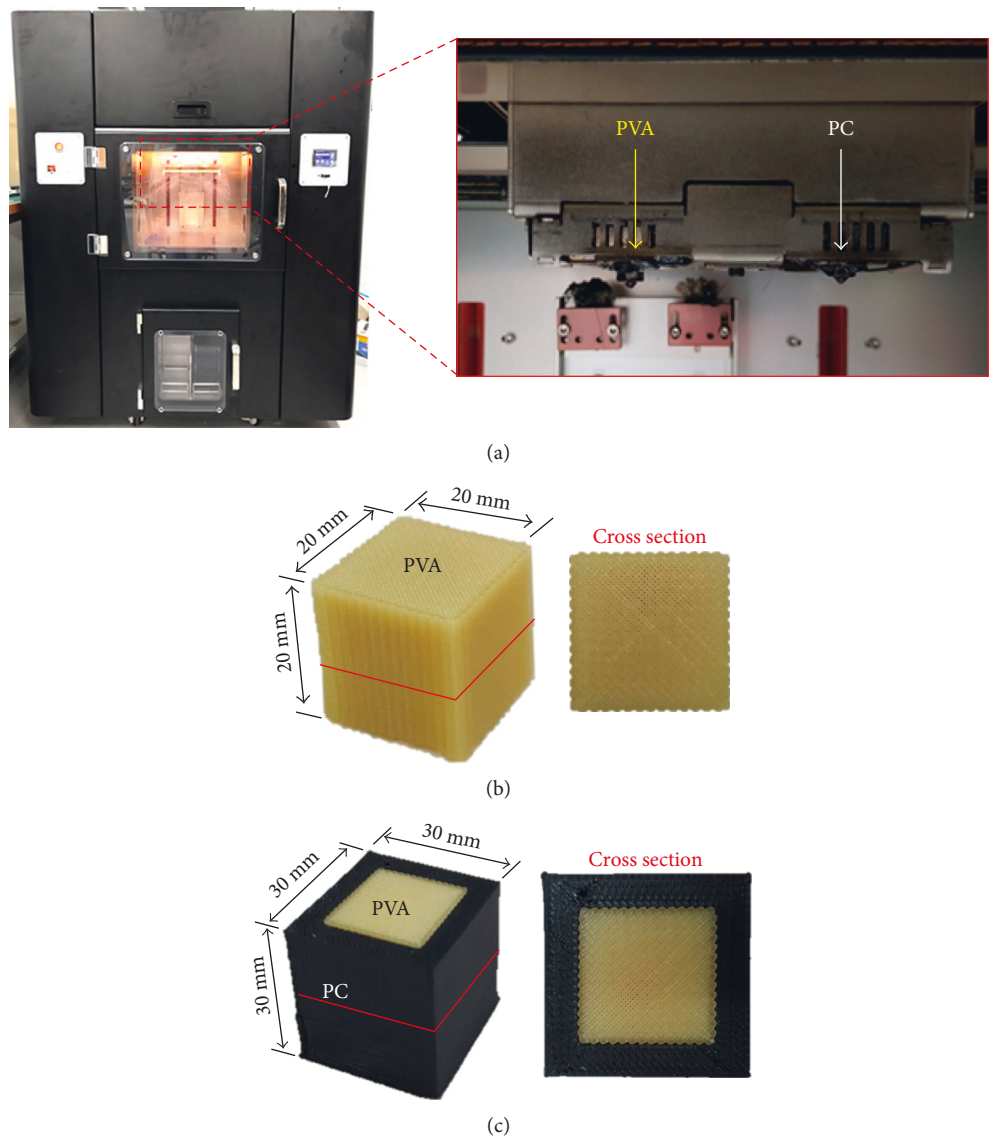

Figure 2: (a) FDM machine equipped with dual extruders and a thermostatic control chamber. 3D printed cubic samples for the solubility test of (b) external- and (c) internal-type supports.

equipped with dual extruder modules that could print two different materials for a single part. Specifically, the 3D printer included several thermostatic control systems to modulate the environmental conditions of printing, such as the temperature of the surrounding air in the printing chamber. The use of temperature-controlled conditions in not only the nozzle but also in the chamber instead of room temperature was necessary in order to stably print and integrate 3D structures without defects or delamination in the final product. Table 1 shows the optimal conditions for the 3D printing of PC and PVA filaments, which were used for the build and support materials, respectively. With these process parameters, defect-free parts could be fabricated in the developed FDM machine.

For solubility tests, the 3D printed cubic samples with PVA-only and PC/PVA-combined composition were prepared as shown in Figures 2(b) and 2(c), respectively. We selected two different types of support structures, that is, external and internal ones, as shown in Figure 1. The external supports are needed below build structures that have an undercut or overhung shape (e.g., a "T" shape). Typically, since most surfaces of external supports could be exposed to solvent, they are relatively easy to remove by dissolution.

Table 1: Experimental conditions of FDM-based 3D printing of PVA and PC filaments for the solubility test.

Printing conditions	PVA filament	PC filament
Nozzle temperature	220°C	240°C
Chamber temperature	100°C	
Nozzle speed	80 mm/s	
Fill density	80%, 50%	100%
Layer height	0.2 mm	
Nozzle diameter	0.4 mm	

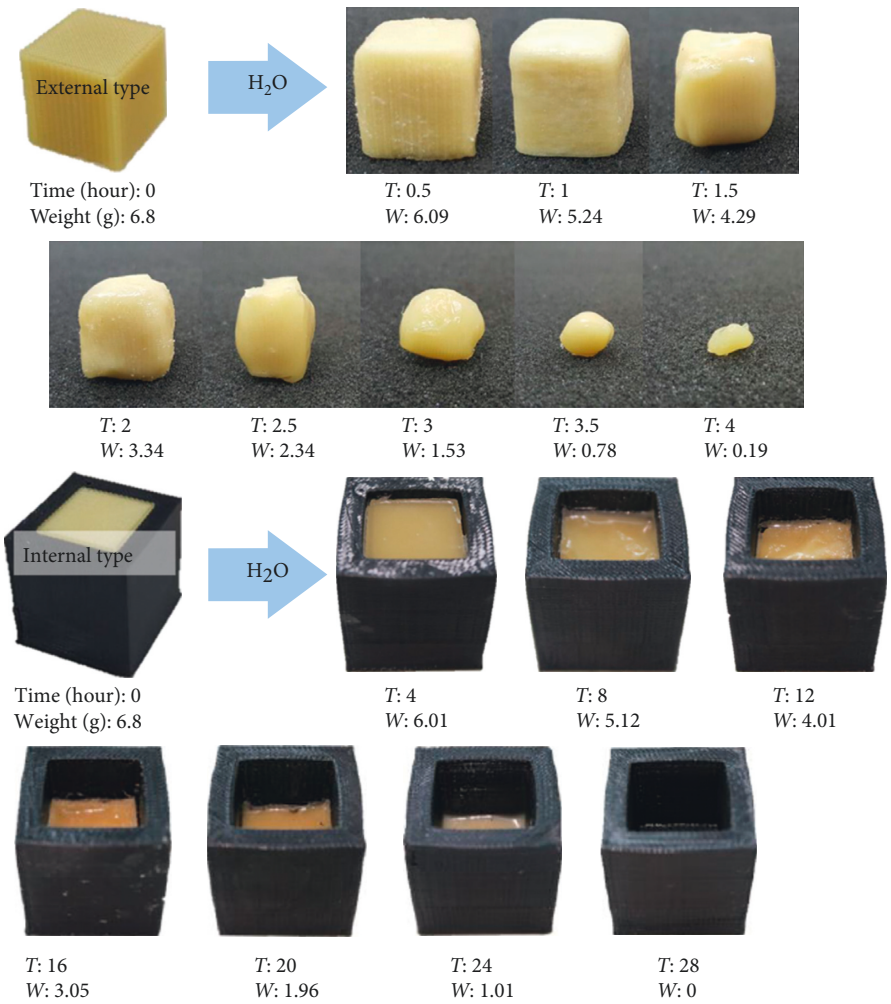

Figure 3: Experimental results of the dissolution of PVA supports in distilled water.

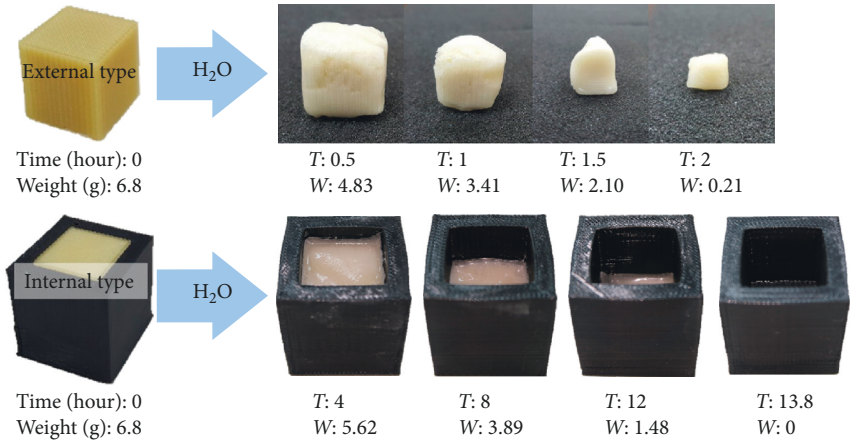

Figure 4: Experimental results of the dissolution of PVA supports in hydrogen peroxide.

Meanwhile, internal-type supports should be essentially matched to the build structures with cavities or hollows. Due to their limited surface area that is exposed to the solvent, it generally takes more time to dissolve out the support within the build part. With the assumption of a difference in the exposed area of support surfaces, we designed a fully exposed PVA part and a PC-surrounded PVA part with one exposed surface, which corresponded to external and internal supports, respectively. As shown in Figure 2, both types of samples, especially those with internal supports,

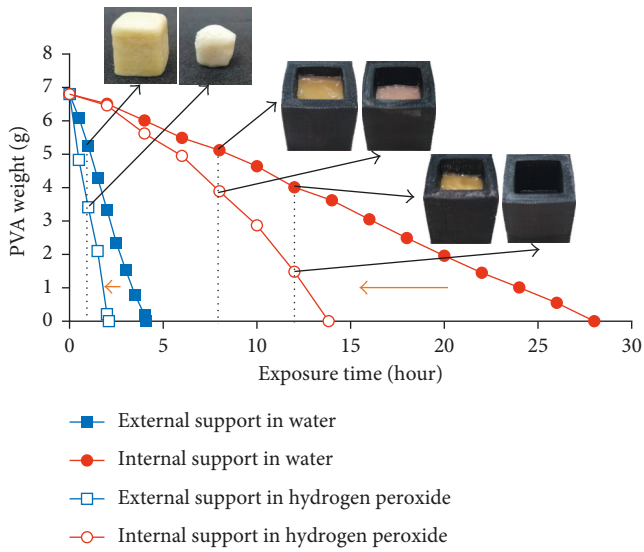

Figure 5: Dissolution rates of external- and internal-type PVA support samples in water and hydrogen peroxide.

could be fabricated with good reproducibility using the process conditions in Table 1.

3.2. Enhanced Solubility in Hydrogen Peroxide with Ultrasonication. Using the as-prepared samples, we first tested the water solubility of the internal- and external-type parts. Figures 3 and 4 present the change in shape and weight of each sample with increasing dissolution time. While the external one was checked every half-hour, the internal one was measured at intervals of four hours due to its relatively low dissolution rate. As a result, it took 246 minutes to totally dissolve out the external-type PVA support with an initial weight of 6.8 g, which corresponded to a dissolution rate of 0.4032%/min. In the case of the internal-type support, it took 1680 minutes for the complete dissolution at a rate of 0.0595%/min, which was slower than that of the external support sample by 6.78 times. These results were essentially expected because of the difference in the exposed surface area. Next, the same samples with internal and external support parts were tested in H_2O_2. The change in shape and weight was measured in the same manner as the water solubility test. In the test of H_2O_2, it took 123 and 830 minutes to completely dissolve the external- and internal-type samples, respectively, corresponding to dissolution rates of 0.8131 and 0.1205%/min, which were overall twice as fast as dissolution in water. Figure 5 displays the dissolution rate of each PVA support in H_2O and H_2O_2. We confirmed the faster removal of both types of PVA supports in H_2O_2 than in H_2O at the same time point.

The superior dissolving power of H_2O_2 compared to H_2O is thought to arise from additional degradation caused by the oxygen ions in the solvent. PVA is well known as a water soluble and hydrophilic polymer. As water molecules penetrate between the polymeric chains of PVA during water uptake, the polymer swells and transitions into a dissolved state due to the weaker hydrogen bonding

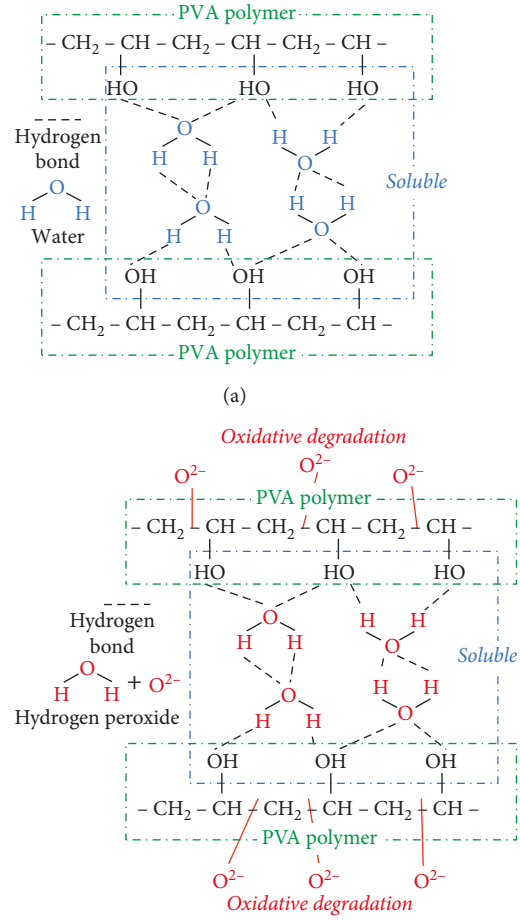

Figure 6: Schematic illustration of the mechanism of the dissolution and degradation of PVA materials by (a) water and (b) hydrogen peroxide.

between the polymer chains (Figure 6(a)) [18–20]. In addition to the water solubility, the degradation of PVA has been studied using photochemical, electrochemical, and photocatalytic methods for consideration as a waste removal technique [21–24]. Those studies suggested that PVA degradation was accelerated by adding H_2O_2 into the reaction process, where more reactive species including hydroxyl and peroxyl radicals were generated and the scission of polymer chains occurred more actively [16–18, 24]. We experimentally confirmed that the dissolution of PVA in H_2O_2 was considerably enhanced compared with the process conducted in water. Such enhancements were thought to be attributable to oxidative degradation induced by the reactive radicals, which would influence the dissolution synergistically with the weakening of hydrogen bonding (Figure 6(b)).

To further confirm the PVA removal efficiency, EDX analysis was performed using four types of 3D printed samples: one each composed of PVA and PC and two composed of PC-PVA complexes. These samples were dissolved separately in H_2O and H_2O_2 (Figure 7). Since PVA is a relatively oxygen-rich polymer, as expected, the PVA

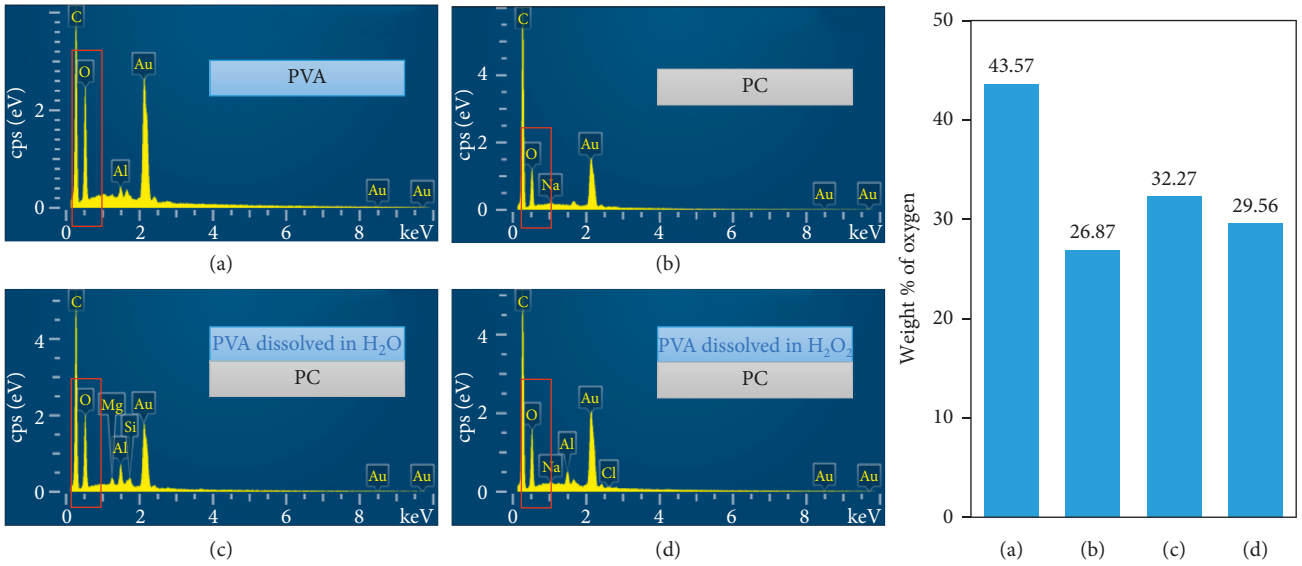

Figure 7: EDX spectra including comparative oxygen peaks on the surface of (a) PVA, (b) PC, and PC-PVA specimens after PVA dissolution in (c) H_2O and (d) H_2O_2. The red boxes in (c) and (d) indicate oxygen peaks. The histogram on the right indicates the weight composition of oxygen in each specimen.

sample shows a higher peak and weight content of oxygen element than the PC sample in their EDX spectra and their semiquantitative element composition data, respectively, as shown in Figures 7(a) and 7(b). Both of the PC-PVA samples dissolved in H_2O and H_2O_2 (Figures 7(c) and 7(d)) showed slightly higher oxygen content than the PC-only sample (Figure 7(b)). These findings were attributed to possible residue of PVA stuck onto the surface of PC even after dissolution because the FDM-based printed parts essentially had numerous tiny ridge-grooves on their surface. Comparing the two samples with each other indicated that the H_2O_2-treated sample had an oxygen content that was lower and more similar to the PC sample than the H_2O-treated one, as shown in the data in Figures 7(c) and 7(d). This implies that H_2O_2 dissolution was more effective than H_2O treatment in terms of PVA removal.

Next, we tried to further enhance the dissolution of H_2O_2 by applying ultrasonication during the dissolution process of PVA. Figure 8 displays the comparison of the dissolution processes depending on whether sonication treatment was employed on the H_2O_2 solvent. Under ultrasonication, the external- and internal-type PVA supports were completely removed in approximately one and nine hours, respectively. These corresponded to dissolution rates of 1.67 and 0.1851%/min, which were faster by 2.05 and 1.54 times compared to those under static conditions in the same solvent. In the field of chemical engineering, ultrasonication has proved its advantageous effects on the degradation or dispersion of substances in some solvent systems [25, 26]. The results in this experiment were in agreement with the previous works addressing the accelerating effect of ultrasonication on polymer dissolution or degradation. The high-energy ultrasonic wave was thought to contribute to the aforementioned mechanisms

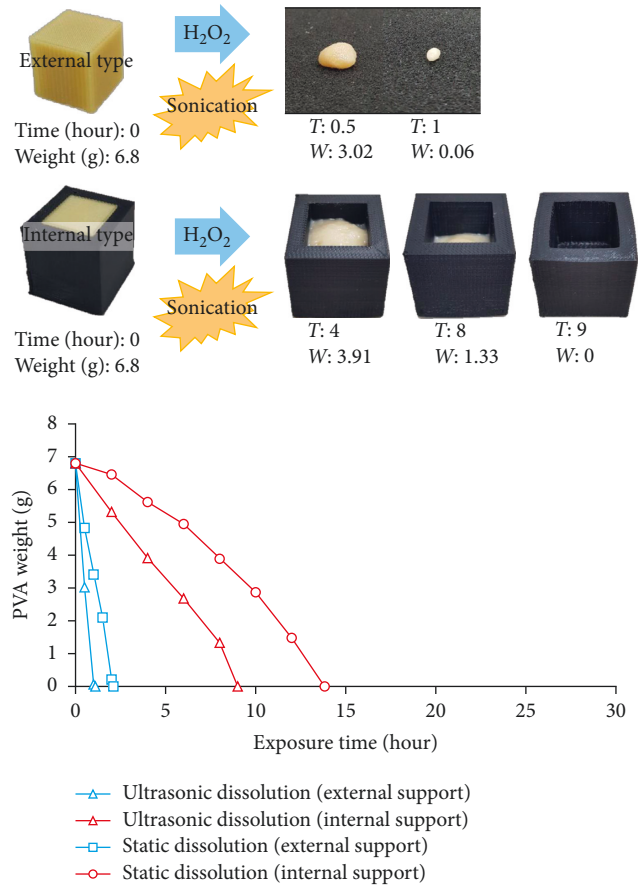

Figure 8: Dissolution rates of external- and internal-type PVA support samples in hydrogen peroxide with and without application of ultrasonication.

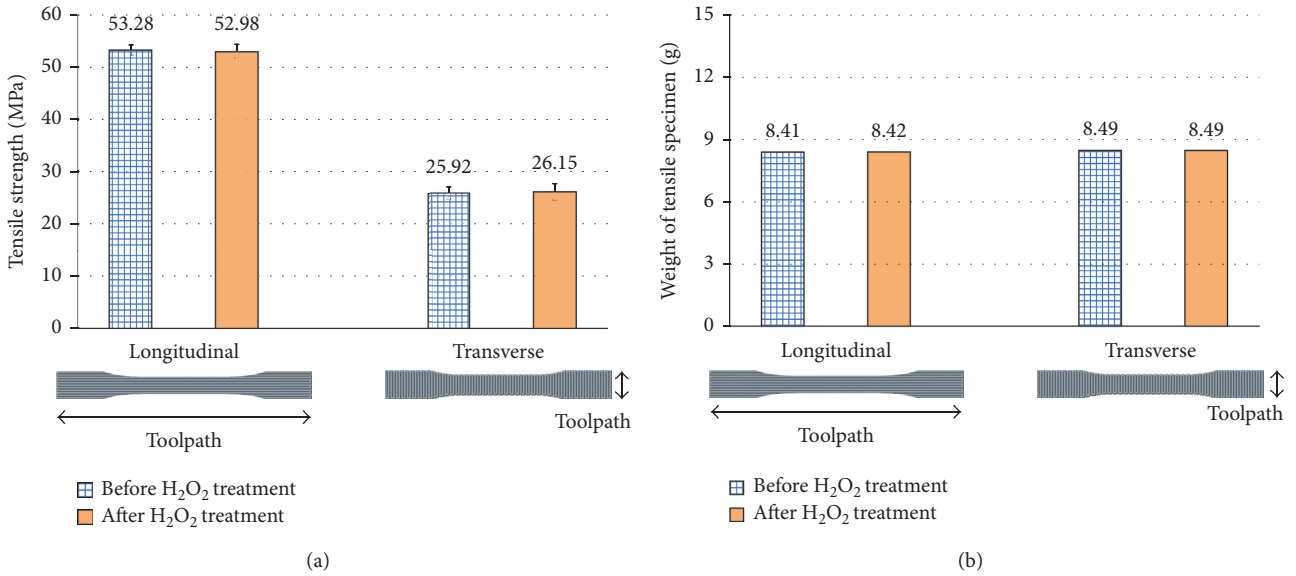

FIGURE 9: Change in (a) tensile strength and (b) weight of direction-varied specimens after H_2O_2 treatment. In the tensile tests in (a), three specimens were tested in each experiment, and the tensile strength is shown as the mean ± standard deviation.

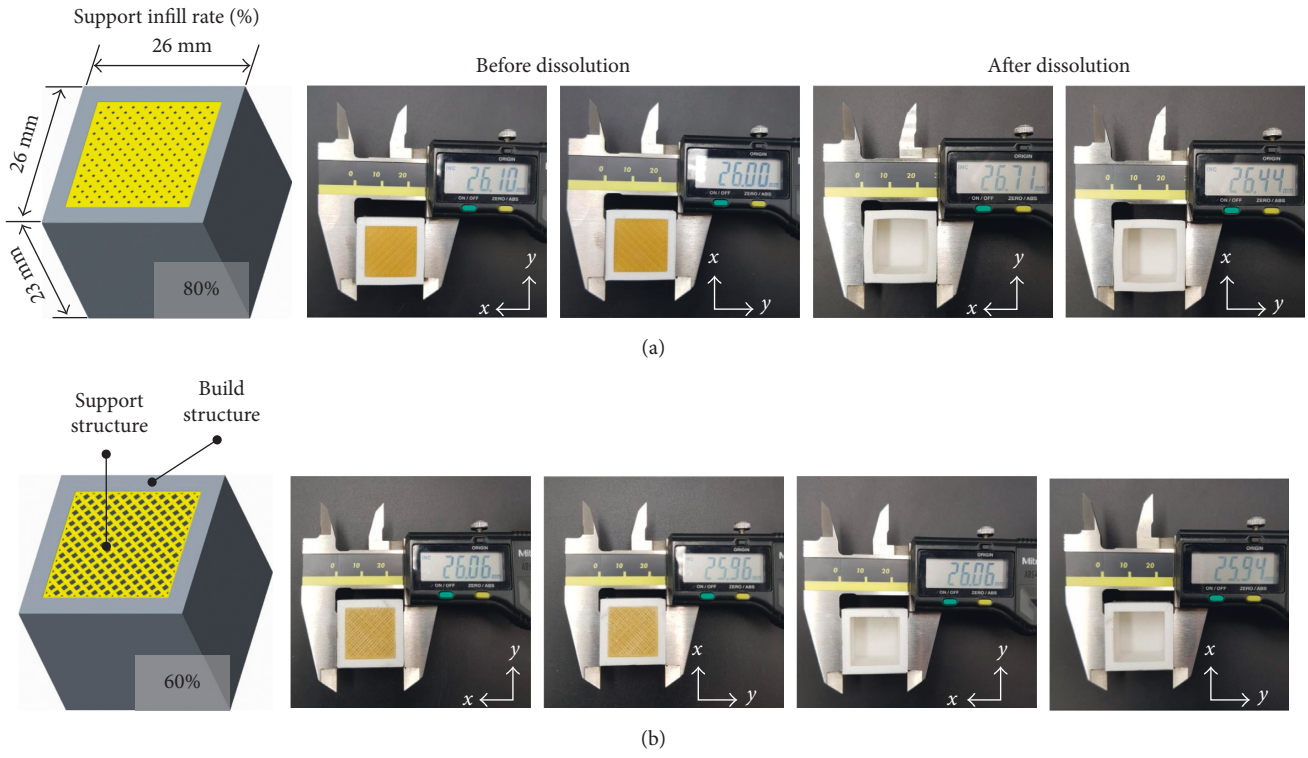

FIGURE 10: Evaluation of dimensional change before and after dissolution in two different specimens with (a) 80% and (b) 60% of support infill rate.

of oxygen-based degradation and water penetration. From the experimental results, we could clearly confirm the feasibility of the physicochemical method for PVA dissolution using H_2O_2 and sonication treatment.

3.3. Sustainable Properties of Support Removal Treatment. After the support removal process mentioned above, the build part should not be influenced by the reactive dissolution conditions, that is, H_2O_2 and ultrasonication. To analyze the effect of the dissolution conditions on the build part, two types of PC specimens were prepared for tensile testing as shown in Figure 9. Typically, FDM-printed parts show mechanically anisotropic properties that are dependent on the direction of the printing toolpath. Similarly, Figure

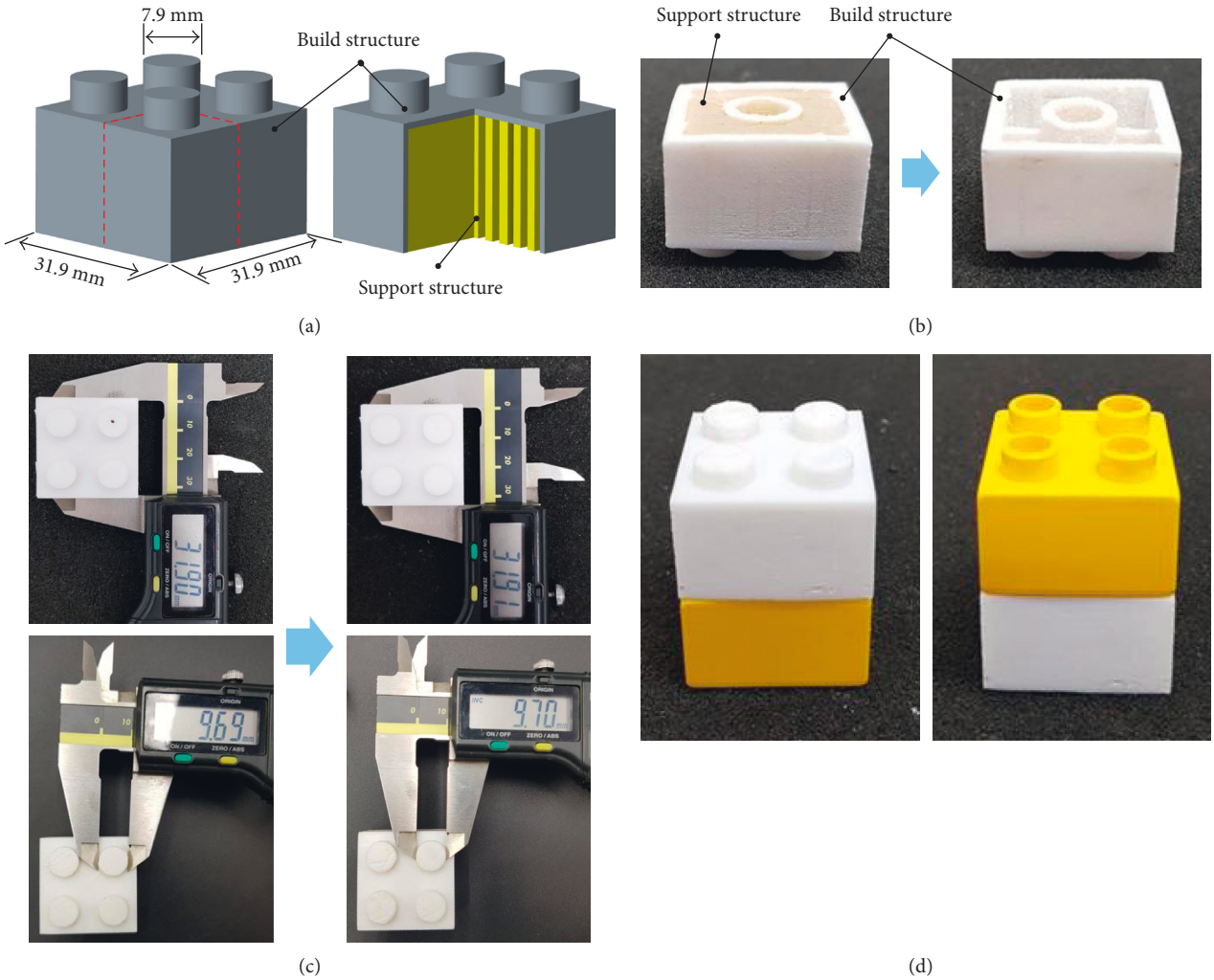

Figure 11: (a) A CAD model of a Lego structure composed of build and support parts. (b) The dual-printed structure including a PC build part and a PVA support part. (c) Comparison of the dimensions of the printed part before and after dissolution of the PVA support. (d) Assembly of the H_2O_2-treated part with an original Lego part with an identical shape.

9(a) displays the different tensile strengths of the PC specimens that were separately printed in the longitudinal and transverse directions with respect to the direction of the tensile load. The longitudinal and transverse specimens provided average tensile strengths of 53.28 and 25.92 MPa, respectively. After soaking the specimens for two hours in H_2O_2, the tensile strengths of longitudinal and transverse specimens were 52.98 and 26.15 MPa, respectively, which were not changed compared with the values of the untreated specimens. In addition to the intact mechanical properties, there was no weight loss between the specimens before and after the H_2O_2 treatment, as shown in Figure 9(b).

Figure 10 displays the evaluation of dimensional change before and after H_2O_2 dissolution using two different build-support parts with 80% and 60% of support infill rate. When the build-support part with 80% of inner support was immersed in H_2O_2 for 9 hours, the build part exhibited a slight distortion (Figure 10(a)), which might be possibly due to support swelling and H_2O_2 infiltration. When the infill rate of support part was reduced to 60%, the support dissolution was completed in 5 hours, and we could obtain a negligible change of dimensions (Figure 10(b)). We also evaluated the dimensional change using a practical part, as shown in Figure 11. We designed a Lego structure with an internal cavity. For more effective exposure to dissolving agent, the internal support structure was designed as an alternately half-filled shape, thereby enabling facile and fast dissolution (Figure 11(a)). Figure 11(b) shows the resulting printed part according to the dual-part design and its removed PVA part after H_2O_2 dissolution for 50 minutes. It was confirmed that there was no dimensional change during the support removal process, as shown in Figure 11(c). Owing to the pristine dimensions of the postprocessed part, Figure 11(d) reveals that it could be well assembled with the original Lego part with a reference shape that was identical to the CAD model at the design step. Overall, we demonstrated the feasibility of the removal of a PVA support part in terms of the intactness of the geometry and the mechanical properties.

4. Conclusion

To render stable 3D architecture in FDM-based 3D printing, a support structure has to be effectively formed along with the shape of the build part. The present study has indicated our initial effort to use the reactivity of H_2O_2 in conjunction with ultrasonication for efficient dissolution of PVA structures. PVA has been widely utilized as a water-soluble support material in the field of 3D printing. To the best of our knowledge, the application of a physicochemical method to remove a PVA-based support in 3D printing process has seldom been reported to date. Two different type samples composed of PVA and PVA-PC, which were used as representative samples with external and internal supports, respectively, were tested under several conditions depending upon the application of H_2O_2 and ultrasonication. When comparing this method with normal water-based dissolution, we confirmed a greater than two times enhancement in the dissolution rate and even a four times enhancement in the case of an external-type support. In addition, the applicability of the reactive method was confirmed based on the unaltered properties in terms of mechanical strength and shape geometry. These results collectively suggest that the proposed method has the potential to enhance the productivity of the support removal process and overcome obstacles of intractable supports with complicated shapes. On the basis of the results presented here, further studies with other FDM-applicable materials are underway to evaluate the feasibility of the suggested method in 3D printing applications.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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