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Strength Development Characteristics of SBR-Modified Cementitious Mixtures for 3-Demensional Concrete Printing

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Abstract: The properties of normal cementitious mixtures currently employed to the construction projects cannot be used to the three-dimensional concrete printing technology. This study experimentally investigated the compressive and flexural strength development of styrene-butadiene rubber (SBR)-modified cementitious mixtures for use as basic three-dimensional concrete printing (3DCP) materials. The SBR/cement ratio was a variable of the mix proportion used to produce cast and printed specimens. Experiments were conducted using these specimens to determine the compressive and flexural strength levels of the SBR-modified cementitious mixtures. The results indicated that the compressive strengths of the SBR-modified cementitious mixtures proposed in this study were never less than those of existing 3D concrete printing materials previously introduced for 3DCP applications. It was confirmed that the addition of SBR latex effectively improved the strength of the cementitious mixtures because the relative compressive and flexural strengths increased with increases in the SBR/cement ratio. Moreover, the higher early (i.e., 1-day) strength indicates that the SBR-modified cementitious mixtures would be advantageous to the 3DCP process. However, the compressive and flexural strengths of the printed specimens were weaker than those of the cast specimens.

Keywords: 3DCP; SBR-modified cement mixtures; SBR/cement ratio; compressive strength; flexural strength; cast specimen; printed specimen

1. Introduction

Concrete is still the most widely used construction material worldwide, even though high-performance construction and industrial materials are continuously being developed alongside advances in the materials industry, due to sustainable design and construction. Naturally, formwork installation is necessary for curing fresh concrete. However, such formworks cost a great deal in terms of material, human labor, and equipment resources. Furthermore, the current construction industry is facing challenges, such as low construction productivity, increased construction cost, dangerous work zone, etc. [1]. Many of these environmental issues can be addressed by using three-dimensional concrete printing (3DCP) technology, which is emerging as an innovative new solution in the construction industry. The 3DCP-based automated construction method provides various advantages, such as reducing construction costs and time and providing an eco-friendlier approach [2]. The 3DCP process falls into the category of additive manufacturing, where materials are stacked layer by layer to construct concrete structures, without any assembly process. Unlike existing construction methods where concrete is cast using a formwork, 3DCP is a combined solution employing emerging technologies and materials science, allowing free-form construction without the formwork process [3]. This 3D printing technology is also attracting significant attention in the construction industry, due to the rapid construction it makes possible [4].

When compared to conventional construction technologies, 3DCP is viewed as a sustainable design solution that provides almost unlimited possibilities for implementing geometrically complex designs. The technology is also advantageous in various ways, such as in reducing construction cost and time, minimizing environmental degradation, and eliminating injuries and deaths at construction sites. It should also be noted that the technology can streamline environmentally friendly construction processes, reduce industrial waste, and contribute to reducing energy consumption resulting from producing the raw materials used in formwork [5]. To ensure the sustainability of 3DCP technology, it is necessary to develop not only new materials applicable to the 3DCP process, but also environmentally friendly concrete materials. Existing concrete materials currently being employed in the construction field are unsuitable for 3DCP applications because of their properties. Consequently, research is underway worldwide to develop concrete printing materials applicable to the 3DCP process [2]. Recent studies on such materials have used ordinary Portland cement as basic material and were conducted using silica fume [6–8], fly ash [1,9,10], and silica fume and fly ash [10,11], but no work to date has used water-soluble polymers, such as styrene-butadiene rubber (SBR) as modifiers.

Hence, in this study, polymer-modified cementitious mixtures were produced by adding organic polymers that were emulsified (or re-dispersed) in the water whilst mixing Portland cement with other raw materials [12–14]. When polymer particles are dispersed in a mixture, they behave like ball bearings, facilitating the relative motion of cement particles against hydration particles [15]. Surfactants contained in the polymer latex act in a similar manner, improving the physical and chemical performances of cement mixtures [16–18]. This type of water-soluble polymer contributes to cultivating the performance of cementitious mixtures, improving their cost-effectiveness and extending the scope of their application as construction materials.

SBR latex is one of the most widely used water-soluble polymers in the world. Despite that, not a single study has been conducted on SBR latex-modified mixtures for use as 3DCP materials. In other words, the idea of using SBR latex as an admixture in cementitious mixtures intended for 3DCP applications is unique to the present study. Moreover, previous research on 3DCP materials has mostly focused on demonstrating the feasibility of the proposed printing materials, and thus, many of these studies were conducted on an ad hoc basis. This means that the development of printing materials is still in an early stage in terms of technological maturity, and developing such 3DCP materials requires an accurate assessment of their strength properties. Therefore, the compressive and flexural strengths of SBR-modified cementitious mixtures that SBR latex as an admixture was employed for improving the properties of existing cementitious mixtures were experimentally investigated whether it can be structurally sustainable as a 3DCP material. This is the motivation of this study. In other words, this research experimentally investigated sustainable materials for use in 3DCP applications by assessing the compressive and flexural strength development of SBR-modified cementitious mixtures, thereby contributing to the advancement of 3DCP technology.

2. Experimental Program

2.1. Materials

This study used ordinary Portland cement, silica sand, fly ash, silica fume, superplasticizer, and viscosity modifying agents. Their characteristics are outlined below. The features of SBR latex, the key material in the present study, are summarized in Table 1, and its chemical constitution is illustrated in Figure 1.

- Ordinary Portland cement (Type I): Density 3.14 (g/cm^3), Fineness 3630 (cm^2/g)
- Silica sand: Particle size 0.08 (mm), Apparent density 1.57, Purity 97.3 (%)
- Fly ash: Density 2.22 (g/cm^3), SiO_2 51.9 (%), Specific surface 3651 (cm^2/g)
- Silica fume: SiO_2 96.7 (%), Bulk density (undensified) 200–350 (g/cm^3), Specific surface 157,700 (cm^2/g)
- Superplasticizer: Specific gravity 1.05 ± 0.05 (20 °C), Alkali ≤ 0.01(%), Chloride ≤ 0.01(%)
- Viscosity modifying agent: White powder, Bulk density 430 (kg/m^3), Particle size (0.074 mm) ≥ 95%

Table 1. Properties of styrene-butadiene rubber (SBR) latex.

Total Solids (%)	pH	Viscosity (mPa·s)	Surface Tension (dynes/cm)	Specific Gravity (20 °C)	Minimum Film Forming Temperature (°C)
47–50	9.9–10.5	40	30–35	1.01 ± 0.01	<4

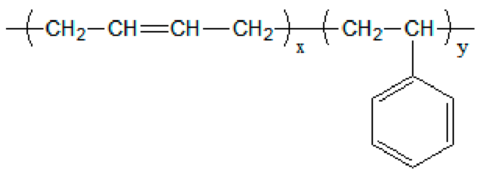

Figure 1. Chemical constitution of SBR latex.

2.2. *Specimen Preparation*

2.2.1. Mix Proportion

In this study, the properties of fresh SBR-cementitious mixtures applicable to the 3DCP process were determined through a trial-and-error procedure. As a result, the optimal flow was determined to be 70% ± 1%. The water/cement ratio was controlled by considering the SBR/cement ratio needed to achieve this optimal flow of 70% ± 1%. The optimal mix proportion was determined based on the results of the trial-and-error procedure. These results indicate that the water/cement ratio allowing the optimal flow to be reached ranged from 0.398 to 0.452, and this figure decreased with increases in the SBR/cement ratio. The optimal flow for 3DCP applications determined in this study (i.e., 70% ± 1%) may be deemed very small given that the standard flow applied when producing compressive strength test specimens of cement mortar under ASTM C109/C109M-02: Testing Method for Compressive Strength of Hydraulic Cement Mortar is 110% ± 5% [19].

Here, the SBR/cement ratio was determined based on the number of total solids, while the water/cement ratio was estimated considering the amount of water contained in the SBR latex. The optimal mix proportions were calculated based on these results, as shown in Table 2. Aside from the materials described in this mix proportion table, a superplasticizer and viscosity modifying agent were also added; their amounts were 1% and 0.05% of the cement weight, respectively.

Table 2. Mix proportions of SBR-modified cementitious mixtures (unit: wt.%).

SBR/Cement Ratio	Water/Cement Ratio	SBR	Water	Cement	Silica Sand	Fly Ash	Silica Fume
0	0.452	0	11.24	24.85	53.25	7.10	3.55
0.05	0.448	1.23	11.00	24.58	52.66	7.02	3.51
0.10	0.441	2.43	10.73	24.31	52.10	6.95	3.47
0.15	0.436	3.61	10.48	24.05	51.55	6.87	3.44
0.20	0.398	4.80	9.54	23.99	51.40	6.85	3.43

2.2.2. Specimen Production

In this study, two types of test specimens (i.e., cast and printed) were prepared. The cast specimens were intended to simulate conventional formwork-based casting construction methods, while printed specimens were included to simulate 3D printing-based additive construction. The cast specimens were produced in accordance with the standard methods under ASTM C348-14: Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars [20]. The standard flow was, however, set to 70% ± 1% instead of 110% ± 5%. The printed specimens were produced using the same mix proportion and standard flow as applied to the production of the cast specimens. To be more specific, printing was directly conducted inside the mold, as shown in Figure 2, and the specimen dimensions were 40 × 40 × 160 mm. No compacting operations were conducted afterward. Mixture printing was performed using a peristaltic pump and a custom-made extrusion-based concrete printer equipped with a nozzle (36 × 10 mm). The two types of specimens were both subject to curing in a constant temperature and humidity chamber at a temperature of 23 °C ± 2 °C and humidity of 65% ± 5%, and were collected at different curing ages.

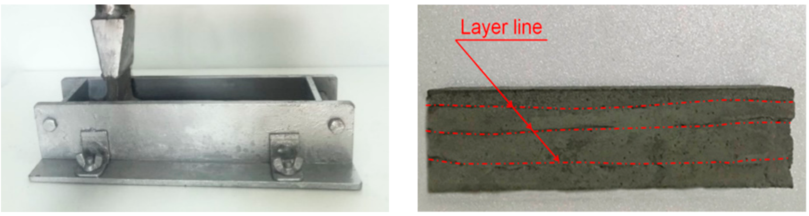

Figure 2. Production of printed specimens.

2.3. Test Methods

2.3.1. Compressive Strength

Both portions from each prism broken in the flexural strength tests were used as specimens for the compressive strength tests. Testing was conducted in accordance with ASTM C349-18: Standard Test Method for Compressive Strength of Hydraulic-Cement Mortars [21]. For this compressive test, three specimens that had no defect were selected from both portions from each prism broken in flexural. A UTM (INSTRON 8502) was employed, and the compressive strength estimated using Equation (1).

$$f_c = P\ /\ A \tag{1}$$

where f_c = Compressive strength (MPa), P = Maximum load (N), and A = Cross-sectional area of the specimen (mm^2).

2.3.2. Flexural Strength

Flexural strength testing was conducted in accordance with ASTM C348-14: Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars [20]. Three prism specimens shall be made for each period of test specified. The testing was conducted using the same UTM employed in the compressive strength tests, and the flexural strength was estimated using Equation (2).

$$f_b = 6M\ /\ bd^2 \tag{2}$$

where f_b = Flexural strength (MPa), M = Maximum flexural moment (N·mm), b = Width of the specimen's cross-section (mm), and d = Height of the specimen's cross-section (mm).

3. Results and Discussion

3.1. Compressive Strength

3.1.1. Compressive Strength of Cast Specimens

The compressive strength of the cast specimens was measured with respect to the curing age and SBR/cement ratio, and the results are presented in Figure 3. For the cast specimens, the 1-day compressive strength ranged from 9.1 MPa to 21.7 MPa, while the 28-day compressive strength ranged from 43.5 MPa to 63.2 MPa. It was also found that the 28-day compressive strengths were 43.5 MPa and 63.2 MPa when the SBR/cement ratio was 0 and 0.20, respectively; the compressive strength tended to increase with increases in the SBR/cement ratio.

In a similar study on compressive strength properties, Chandra et al. [15] reported that the compressive strength ranged from 15 MPa to 29 MPa and 17 MPa to 32 MPa when the SBR/cement ratio was 0.10 and 0.20, respectively. Barluenga et al. [22] presented compressive strengths of 21 MPa to 34 MPa and 22 MPa to 36 MPa when the SBR/cement ratio was 0.10 and 0.20, respectively. These results indicate that the compressive strength increased with increases in the SBR/cement ratio. Similar trends can also be found in other studies [23–25].

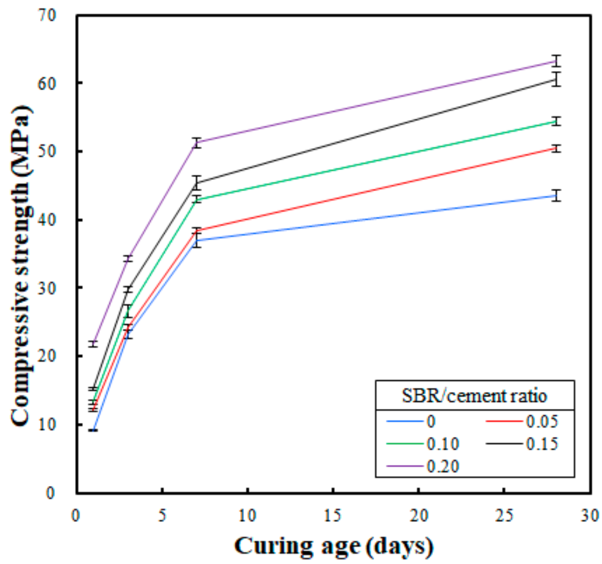

Figure 3. Comparison of cast specimens' compressive strength test results for different SBR/cement ratios.

With the 28-day compressive strength set as a reference (i.e., 100%), the compressive strength development rates of the cast specimens were plotted against the SBR/cement ratios, as shown in Figure 4. At 1-day, the compressive strength development rate was 21% without the SBR latex addition; the addition increased the figure to between 24% and 34%. At the 7-day age, the figure was 85% without the SBR latex addition, and decreased to 76 to 81% with the SBR latex addition.

To determine the effect of the addition of SBR latex on the compressive strength of the cast specimens, their relative compressive strengths were determined and compared; an SBR/cement ratio of zero was set as a reference (i.e., 100%). As shown in Table 3, the relative compressive strengths ranged from 116 to 145%. This result is comparable to that of Chandra et al. [15], who reported that the relative compressive strengths of SBR-modified cementitious mixtures ranged from 123 to 146% when the SBR/cement ratio was increased from 0.05 to 0.20.

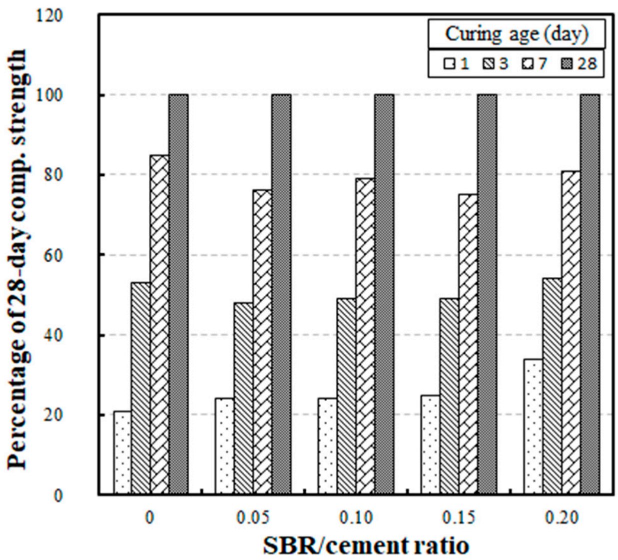

Figure 4. Relative gains in compressive strength and SBR/cement ratios for cast specimens with different curing ages.

Table 3. Cast specimen compressive strength test results at 28-days.

SBR/Cement Ratio	0	0.05	0.10	0.15	0.20
Compressive strength (MPa)	43.50 (0.89)*	50.43 (0.49)*	54.33 (0.60)*	60.56 (0.94)*	63.28 (0.85)*
Relative compressive strength (%)	100	116	125	139	145

*( ) is standard error.

In the present study, the 28-day compressive strengths of the SBR-modified cementitious mixtures was found to reach 63.2 MPa, which is two to three times stronger than what was achieved in previous research. These results are thought to be associated with the addition of silica fume. In the present study, silica fume was used. The reference compressive strength (i.e., the compressive strength when the SBR/cement ratio was zero) was relatively high at 43.5 MPa, especially as compared to the 20 MPa reported by Chandra et al. [15]. This is likely due to the addition of silica fume. Previous studies have also reported that the combined use of silica fume and SBR latex contributed to improving various other performance indexes of concrete [25–27]. This is attributed to the complex effects of the following two factors. First, the interaction between SBR latex and cement hydrates forms films in the microstructure of SBR-modified cement mixtures, improving their strength and durability [28]. Second, the addition of silica fume provides excellent micropore filling effects and promotes a pozzolanic reaction [25].

3.1.2. Compressive Strengths of Printed Specimens

The compressive strengths of the printed specimens were measured with respect to their curing age and SBR/cement ratio; the results are presented in Figure 5. For the printed specimens, the 1-day compressive strengths ranged from 11.3 MPa to 17.4 MPa, while the 28-day compressive strengths ranged from 35.6 MPa to 43.6 MPa. It was also found that the 28-day compressive strengths were 35.6 MPa and 43.6 MPa when the SBR/cement ratio was 0 and 0.20, respectively. It was noted that the compressive strength tended to increase with an increase in the SBR/cement ratio. The 28-day compressive strengths of the SBR-modified cementitious mixtures was found to reach 43.6 MPa, nearly twice as high than those achieved in previous studies in which silica fume was not used [15,22].

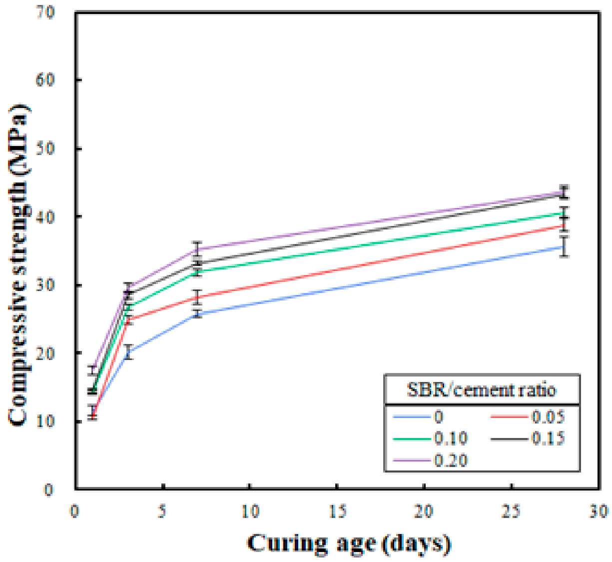

Figure 5. Comparison of printed specimens' compressive strength test results for different SBR/cement ratios.

Figure 6 presents the compressive strength development rate for the printed specimens at different curing ages, with respect to the SBR/cement ratio. With the 28-day compressive strength set as a reference (i.e., 100%), the compressive strength development rate at 1-day age was 32% without the SBR latex addition; the SBR latex addition increased this figure to between 27% and 40%. At the 7-day age, this figure was 72% without the SBR latex addition, increasing to between 73% and 81% with the SBR latex addition.

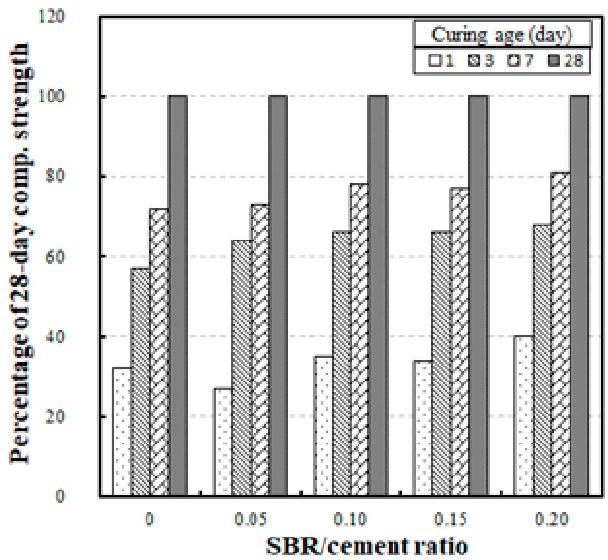

Figure 6. Relative gains in compressive strength and SBR/cement ratios for printed specimens with different curing ages.

To determine the effect of the SBR latex addition on the compressive strengths of the printed specimens, their relative compressive strengths were calculated and compared; the SBR/cement ratio of zero was set as a reference (i.e., 100%). As presented in Table 4, the relative compressive strengths ranged from 108 to 122%. This result is comparable to that of Shete et al. [29], who reported that the relative compressive strengths of printed specimens improved by 114% with the addition of 20% of SBR latex.

Table 4. Compressive strength test results at 28-days using printed specimens.

SBR/Cement Ratio	0	0.05	0.10	0.15	0.20
Compressive strength (MPa)	35.63 (1.39)*	38.78 (0.97)*	40.60 (0.74)*	43.27 (0.73)*	43.64 (0.82)*
Relative compressive strength (%)	100	108	113	121	122

*( ) is standard error.

3.1.3. Relationship of Compressive Strength between Cast and Printed Specimens

The relationship between the cast and printed specimens' compressive strengths was analyzed, as shown in Figure 7. The coefficient of determination (R^2) was determined to be 0.9513, indicating a high correlation between the groups. The slope of the linear regression, however, indicates that the rate of the strength increase was lower in the printed than in the cast specimens. However, due to the high coefficient of determination, the compressive strengths of the printed specimens could be reasonably estimated through the determined linear equation once the compressive strengths of the cast specimens were determined for the SBR-modified cementitious mixtures employed in this study.

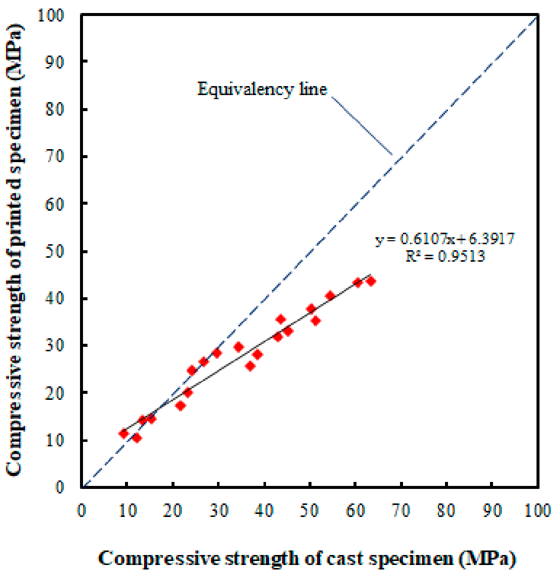

Figure 7. Relationship between cast and printed specimens' compressive strengths.

To assess the difference in compressive strengths between the cast and printed specimens with respect to various SBR/cement ratios, the relative compressive strengths were calculated and compared as presented in Figure 8. It was found that the compressive strengths were relatively lower in the printed than in the cast specimens. To be more specific, the 28-day compressive strengths of the printed specimens were 18% and 31% lower than those of the cast specimens when the SBR/cement ratios were 0 and 0.20, respectively. The lower rate of increase in strength and lower relative compressive strengths of the printed specimens were because compacting operations had not been properly conducted during producing of the printed specimens, and thus their strengths could not be sufficiently developed.

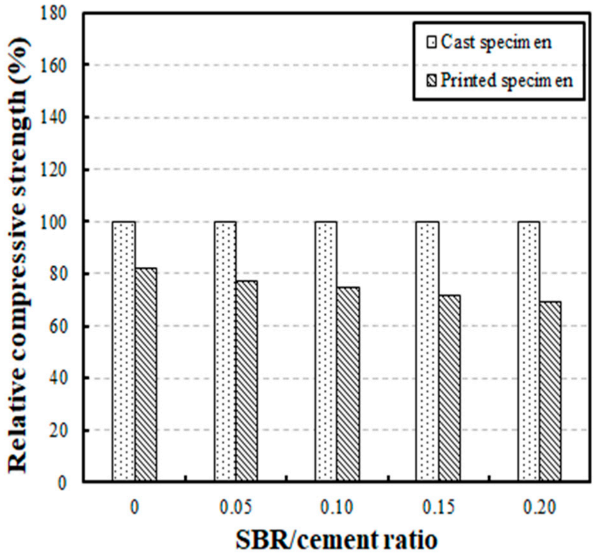

Figure 8. Relative compressive strengths of the cast and printed specimens.

In a previous study similarly conducted on the cast and printed specimens, Marchment et al. [30] reported that the 7-day compressive strength of cement mortar was 34 MPa when using cast specimens (25 mm). When using saw-cut printed specimens (50 × 25 × 30 mm), the compressive strengths ranged from 8.8 MPa to 22.8 MPa, and varied depending on the delay time (i.e., the time interval between printing layers) and loading direction. Nerella et al. [1] also reported that the 21-day compressive strength of cement concrete was 80.6 MPa when using printed specimens; the figure was slightly lower, 73.4 MPa, when using cast specimens. The researchers attributed this result to the effect of the extruding machine applied, which used a high rate of pressure to press the specimens extruded through its conveyors. Thus, whether or not to apply this method is an important issue to consider. Lastly, the compressive strength test results obtained from the SBR-modified cementitious mixtures developed in this study were compared with those attained from various cementitious mixtures previously developed for 3DCP applications. Kazmian et al. [6] reported that in Portland cement-based mixtures mixed with silica fume, fibers, and nanoclay, the 7-day compressive strength was between 31.0 MPa and 35.2 MPa, and the 28-day compressive strength ranged from 44.7 MPa to 49.9 MPa. Malaeb et al. [31] found that in cement-based mixtures composed of cement, sand, high-performance superplasticizers, and retarders, the compressive strengths [32] ranged from 40.6 MPa to 55.4 MPa. Weng et al. [8] placed cement mixtures composed of Portland cement, silica fume, silica sand, fly ash, river sand, and superplasticizers in a mold to produce test specimens, and followed with compressive strength tests conducted in accordance with ASTM C109/C109M-13. The resulting 28-day compressive strength was determined to be 49.7 MPa. The compressive strengths of the cementitious mixtures developed in the present study (50.4 MPa to 63.2 MPa for cast and 38.7 MPa to 43.6 MPa for printed specimens) were never lower than those achieved in previous studies. Thus, the cementitious mixtures developed were deemed to be sufficiently competitive as materials for use in 3DCP applications.

3.2. Flexural Strength

3.2.1. Flexural Strength of Cast Specimens

The flexural strengths of the cast specimens were measured with respect to curing age and SBR/cement ratio; the results are presented in Figure 9. For the cast specimens, the 1-day flexural strength ranged from 5.1 MPa to 10.0 MPa. For the 28-day specimens, flexural strength ranged between 12.7 MPa and 17.8 MPa. It was also found that the 28-day flexural strengths were 12.7 MPa, 13.5 MPa, and 17.8 MPa when the SBR/cement ratios were 0, 0.05, and 0.20, respectively., The flexural strength tended to increase with increases in the SBR/cement ratio.

In a previous study on the flexural strength properties of SBR-modified mortar, Chandra et al. [15] reported that the flexural strengths ranged from 6 MPa to 10 MPa and 7 MPa to 12 MPa when the SBR/cement ratios were 0.10 and 0.20, respectively. Barluenga et al. [15] presented flexural strengths ranging from 4.1 MPa to 7.0 MPa and 5.5 MPa to 8.5 MPa when the SBR/cement ratios were 0.10 and 0.20, respectively. These results indicate that the flexural strength increased with increases in the SBR/cement ratio; similar trends can also be found in other studies [33–39]. The 28-day flexural strengths of the SBR-modified cement mixtures developed in the present study was found to reach 17.86 MPa, 1.5 times to twice as high as those achieved in previous research. This is primarily attributed to the addition of silica fume.

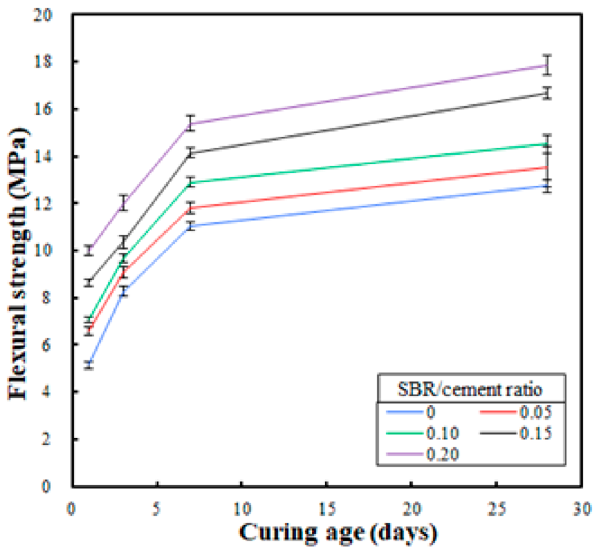

Figure 9. Comparison of cast specimens' flexural strength test results for different SBR/cement ratios.

Figure 10 presents the flexural strength development rates of cast specimens at different curing ages with respect to certain SBR/cement ratios. With the 28-day flexural strength set as a reference (i.e., 100%), the flexural strength development rate at 1-day was 40% without the SBR latex addition; however, the SBR latex addition increased this figure to between 48% and 55%. At the 7-day age, this figure was 86% without the SBR latex addition, and between 84% and 88% with the SBR latex addition.

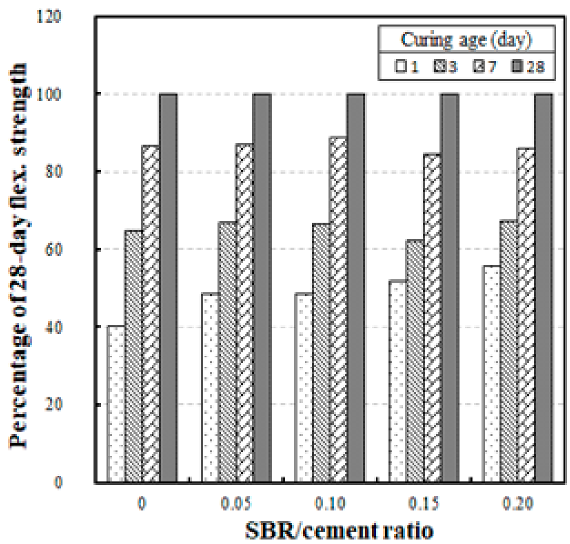

Figure 10. Relative gain in flexural strength and SBR/cement ratios for cast specimens with different curing ages.

To determine the effect of the SBR latex addition on the flexural strength of cast specimens, their relative flexural strengths were calculated and compared; the SBR/cement ratio of zero was set as a reference (i.e., 100%). As presented in Table 5, the relative flexural strengths ranged from 107 to 140%. This significant increase in flexural strength by SBR latex modification is due to the generation of polymer films between the aggregates and the cement particles contained in the cement mixtures, which enhance the binding force between the two groups [39–41]. Also, the increased polymer/cement ratio led to an increase in the volume of the polymer film, thus increasing the flexural strength [42].

Table 5. Flexural strength test results at 28-days using cast specimens.

SBR/Cement Ratio	0	0.05	0.10	0.15	0.20
Flexural strength (MPa)	12.73 (0.28)*	13.56 (0.85)*	14.51 (0.41)*	16.67 (0.24)*	17.86 (0.44)*
Relative flexural strength (%)	100	107	114	130	140

*( ) is standard error.

3.2.2. Flexural Strength of Printed Specimens

The flexural strength of the printed specimens was measured with respect to the curing age and SBR/cement ratio; the results are presented in Figure 11. For the printed specimens, the 1-day flexural strength ranged from 4.7 MPa to 8.8 MPa, while the 28-day flexural strength was between 11.9 MPa and 14.8 MPa. It was also found that the 28-day flexural strengths were 11.9 MPa and 14.8 MPa when the SBR/cement ratios were 0 and 0.20, respectively. The flexural strength tended to increase with increases in the SBR/cement ratio.

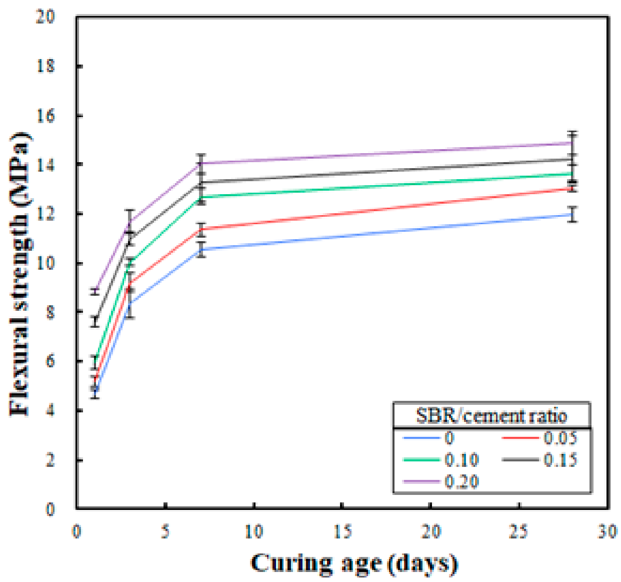

Figure 11. Comparison of printed specimens' flexural strength test results for different SBR/cement ratios.

With the 28-day flexural strength set as a reference (i.e., 100%), the flexural strength development rate at 1-day was 39% without the SBR latex addition; the SBR latex addition altered this figure to between 30% and 59%. At 7-days, this figure was 88% without the SBR latex addition and between 87% and 94% with the SBR addition, as shown in Figure 12.

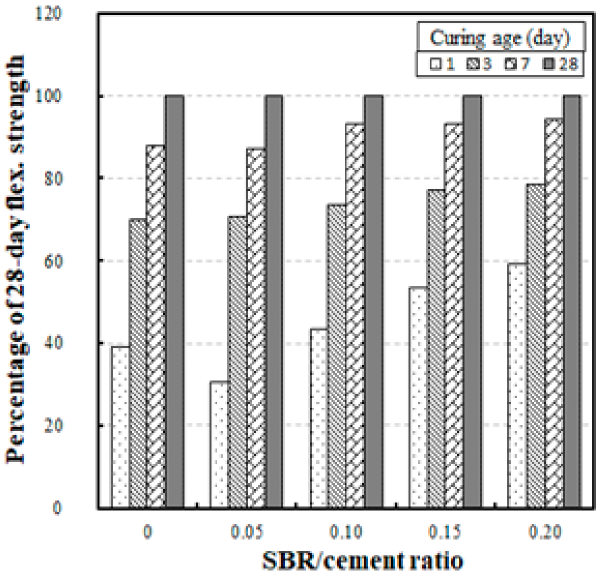

Figure 12. Relative gains in flexural strength and SBR/cement ratios for printed specimens with different curing ages.

To determine the effect of the addition of SBR latex on the flexural strengths of the printed specimens, their relative flexural strengths were calculated and compared; an SBR/cement ratio of zero was set as a reference (i.e., 100%). As summarized in Table 6, the relative flexural strengths ranged from 108 to 124%, increasing with increases in the SBR/cement ratio. However, these figures were lower in the printed than in the cast specimens.

Table 6. Flexural Strength Test Results for Printed Specimens at 28-days.

SBR/Cement Ratio	**0**	**0.05**	**0.10**	**0.15**	**0.20**
Flexural strength (MPa)	11.97 (0.33)*	13.03 (0.11)*	13.65 (0.33)*	14.21 (0.24)*	14.86 (0.47)*
Relative flexural strength (%)	100	108	114	118	124

*( ) is standard error.

3.2.3. Relationship of Flexural Strength between Cast and Printed Specimens

The relationship between the flexural strengths of the cast and printed specimens was analyzed, as shown in Figure 13. The coefficient of determination (R^2) was determined to be 0.9397, indicating a high correlation between the two groups. The slope of the linear regression, however, indicates that the rate of strength increased for the printed specimens and decreased relative to the increasing the rate of strength of the cast specimens. However, due to the high coefficient of determination, the flexural strengths of the printed specimens could be reasonably estimated through the determined linear equation once the flexural strengths of the cast specimens were determined for the SBR-modified cementitious mixtures applied in this study.

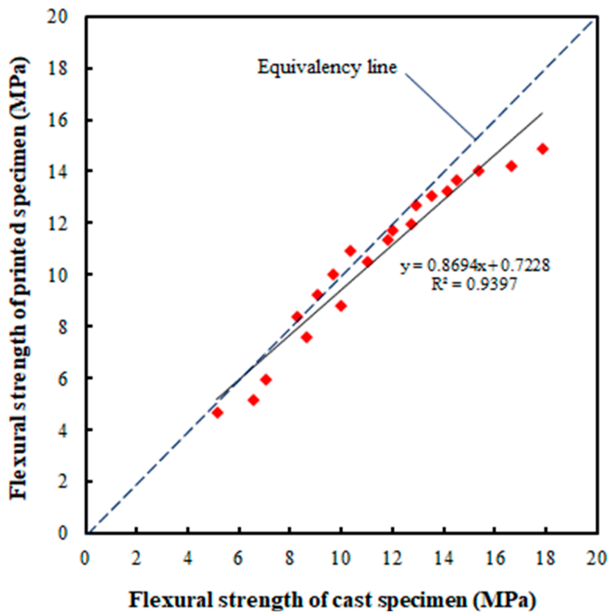

Figure 13. Relationship between cast and printed specimens' flexural strengths.

To assess the differences in flexural strength between the cast and printed specimens with respect to the SBR/cement ratio, the relative flexural strengths were calculated and plotted, as presented in Figure 14. It was found that the compressive strengths were relatively lower in the printed specimens than in the cast. To be more specific, the 28-day flexural strengths of the printed specimens were 6%, 4%, 6%, 15%, and 17% lower than those of the cast specimens when the SBR/cement ratios were 0, 0.05, 0.1, 0.15, and 0.20, respectively. The lower rate of increase in strength and lower relative flexural strengths of the printed specimens were attributed to compacting operations had not been properly conducted during the producing of the printed specimens, and thus their strengths could not be sufficiently developed.

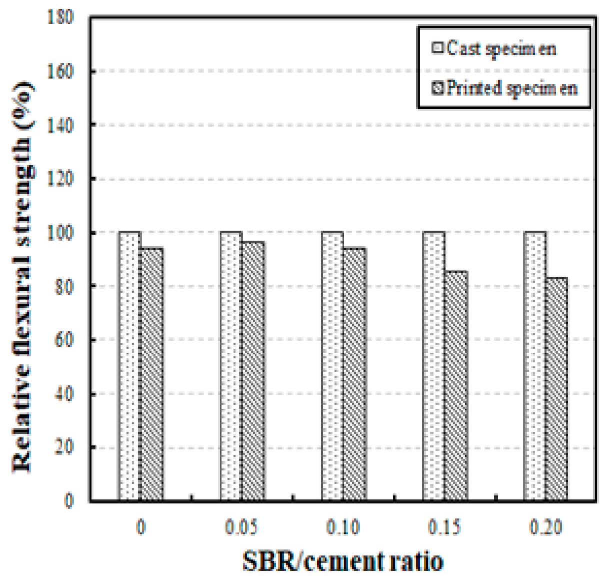

Figure 14. Relative flexural strengths for the cast and printed specimens.

In a previous study on cement mixtures developed for 3DCP applications, Weng et al. [8] produced flexural test specimens (30 × 15 × 350 mm) using a gantry concrete printer. The researchers then conducted four-point flexural tests (with a spacing of 240 mm) on those specimens. The resulting

28-day flexural strength was determined to be 3.7 MPa. Nerella et al. [1] also reported that the 21-day flexural strengths were 5.9 MPa and 5.1 MPa when using printed and cast specimens, respectively. Likewise, the flexural strengths of the cementitious mixtures developed in this study (12.7 MPa to 17.8 MPa for the cast and 11.9 MPa to 14.8 MPa for the printed specimens) were significantly higher than those achieved in previous studies.

4. Conclusions

This study experimentally investigated the compressive and flexural strengths of SBR-modified cementitious mixtures intended for use in 3DCP technology, which is emerging as a sustainable construction solution. The major findings of this study are as follows.

1. Experimental results confirmed that the compressive strengths of the cementitious mixtures ranged from 50.4 MPa to 63.2 MPa and 38.7 MPa to 43.6 MPa when using cast and printed specimens, respectively. The flexural strengths ranged from 12.7 MPa to 17.8 MPa and 11.9 MPa to 14.8 MPa, respectively. These strengths were never lower than those developed for previous 3DCP applications.
2. The strength development rate was measured with respect to curing age. With the 28-day compressive strength set as a reference (i.e., 100%), the compressive strength development rates at 1-day ranged from 24% to 34% and 27% to 40% when using cast and printed specimens, respectively. The flexural strength development rates at 1-day ranged from 48% to 55% and 30% to 59%, respectively. This higher initial strength indicates that the materials developed were suitable for 3DCP operations.
3. The relative compressive strengths were determined with respect to the SBR/cement ratio. The relative compressive strengths ranged from 116% to 145% and 108% to 122% when using cast and printed specimens, respectively. The relative flexural strengths ranged from 107% to 140% and 108% to 124%, respectively. These results confirm that the addition of SBR latex effectively enhanced strength.
4. The strength difference when using the cast and printed specimens widened with increases in the SBR/cement ratio. The compressive strength decreased between 18% and 31%, while the flexural strength decreased between 6% and 17%. For this reason, more attention should be paid to finding ways to narrow this decrease in strength.

Based on these results, it was revealed that compressive and flexural strengths both increased with increases in the SBR/cement ratio, and the rate of strength development was relatively high at earlier curing ages (e.g., at a 1-day curing age). These findings clearly demonstrate the merit of the SBR-modified cementitious mixtures proposed in this study for use as 3DCP materials. In the future, environmentally friendlier 3DCP materials and the durability improvement of 3DCP materials should be studied.

5. Patents

This research is part of the patent application (Application No. 10-2019-0047891) applied for at the Korean Intellectual Property Office.

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References

1. Nerella, V.N.; Mechtcherine, V. Studying the printability of fresh concrete for formwork—Free concrete onsite 3D printing technology (CONPrint3D). In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 16, pp. 333–347.
2. Khoshnevis, B.; Bukkapatnam, S.; Kwon, H.; Saito, F. Experimental Investigation of Contour Crafting using Ceramics Materials. *Rapid Prototyp. J.* **2001**, *7*, 32–41. [CrossRef]
3. Sanjayan, J.G.; Nematollahi, B. 3D concrete printing for construction applications. In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 1, pp. 1–11.
4. Buswell, R.A.; Soar, R.C.; Gibb, A.G.F.; Thorpe, A. Freeform Construction: Mega-Scale Rapid Manufacturing for Construction. *Autom. Constr.* **2007**, *16*, 224–231. [CrossRef]
5. Hager, I.; Golonka, A.; Putanowicz, R. 3D Printing of Buildings and Building Components as the Future of Sustainable Construction? *Procedia Eng.* **2016**, *151*, 292–299. [CrossRef]
6. Kazmian, A.; Yuan, X.; Meier, R.; Khoshnevis, B. Performance-based testing portland cement concrete for construction-scale 3D printing. In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 2, pp. 13–35.
7. Hambach, M.; Rutzen, M.; Volkmer, D. Properties of 3D-printed fiber-reinforced Portland cement paste. In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 5, pp. 73–113.
8. Weng, Y.; Li, M.; Tan, M.J.; Qian, S. Design 3D printing cementitious materials via Fuller Thompson theory and Marson-Percy model. In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 14, pp. 281–306.
9. Rushing, T.S.; Stynoski, P.B.; Barna, L.A.; Al-Chaar, G.K.; Burroughs, J.F.; Shannon, J.D.; Kreiger, M.A.; Case, M.P. Investigation of concrete mixtures for additive construction. In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 7, pp. 137–160.
10. Bentz, D.P.; Jones, S.Z.; Bentz, I.R.; Peltz, M.A. Towards the formulation of robust and sustainable cementitious binders for 3D additive construction by extrusion. In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 15, pp. 307–331.
11. Li, Z.; Wang, L.; Ma, G. Method for the enhancement of buildability and bending resistance of three-dimensional-printable tailing mortar. In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 8, pp. 161–180.
12. Ohama, Y. *Handbook of Polymer-Modified Concrete and Mortars*, 1st ed.; Noyes Publications: Park Ridge, NJ, USA, 1995.
13. ACI-Committee 548. *Polymer-Modified Concrete*; ACI 548.3R-03; American Concrete Institute: Farmington Hills, MI, USA, 2003.
14. Chung, D.D.L. Use of Polymers for Cement Based Structural Materials. *J. Mater. Sci.* **2004**, *39*, 2973–2978. [CrossRef]
15. Chandra, S.; Ohama, Y. *Polymers in Concrete*, 1st ed.; CRC Press: Boca Raton, FL, USA, 1994.
16. Ramakrishnan, V. *Properties and Application of Latex Modified Concrete*, 1st ed.; National Research Council: Washington, DC, USA, 1992.
17. Tukimat, N.N.A.; Sarbini, N.N.; Ibrahim, I.S.; Ma, C.K.; Mutusamy, K. Fresh and Hardened State of Polymer Modified Concrete and Mortars—A Review. *Int. Sym. Civ. Env. Eng.* **2017**, *01025*, 1–10. [CrossRef]
18. Ohama, Y. Polymer-Based Admixtures. *Cem. Concr. Comp.* **1998**, *20*, 189–212. [CrossRef]
19. ASTM C109/C109M-02. Available online: https://www.astm.org/DATABASE.CART/HISTORICAL/C109C109M-02.htm (accessed on 10 July 2019).
20. ASTM C348-14. Available online: https://www.astm.org/DATABASE.CART/HISTORICAL/C348-14.htm (accessed on 10 July 2019).
21. ASTM C349-18. Available online: https://www.astm.org/Standards/C349 (accessed on 10 July 2019).
22. Barluenga, G.; Hernández-Olivares, F. SBR Latex Modified Mortar Rheology and Mechanical Behavior. *Cem. Concr. Res.* **2004**, *34*, 527–535. [CrossRef]

23. Siddiqi, Z.A.; Hameed, M.; Khan, Q.S.; Qazi, J.A. Determination of Compressive Strength and Water Absorption of Styrene Butadiene Rubber (SBR) Latex Modified Concrete. *Pak. J. Sci.* **2013**, *65*, 124–128.
24. Thirumurugan, S.; Sivakumar, A. Synergistic Interaction of Polypropylene Fibers in Latex Modified High Strength Concrete. *Arch. Civ. Eng.* **2013**, *59*, 321–335. [CrossRef]
25. Ahmed, S.F.U. Mechanical and Durability Properties of Mortars Modified with Combined Polymer and Supplementary Cementitious Materials. *J. Mater Civ. Eng.* **2011**, *23*, 1311–1319. [CrossRef]
26. Bache, H.H. Densified Cement/Ultra-Fine Particles-Based Material. In Proceedings of the Second International Conference on Superplasticizers in Concrete, Ottawa, ON, Canada, 10–12 June 1981.
27. Rossignol, J.A. Interfacial Interactions in Concretes with Silica Fume and SBR Latex. *Constr. Build. Mater.* **2009**, *23*, 817–821. [CrossRef]
28. Giustozzi, F. Polymer-Modified Pervious Concrete for Durable and Sustainable Transportation Infrastructures. *Constr. Build. Mater.* **2016**, *111*, 502–512. [CrossRef]
29. Shete, G.N.; Upase, K.S. Evaluation of Compressive Strength and Water Absorption of Styrene Butadiene Rubber (SBR) Latex Modified Concrete. *Int. J. Mod. Eng. Res.* **2014**, *4*, 40–44. Available online: http://www.ijmer.com/papers/Vol4_Issue10/Version-3/F04010_03-4044.pdf (accessed on 10 July 2019).
30. Marchment, T.; Sanjayan, J.G.; Nematollahi, B.; Xia, M. Interlayer Strength of 3D Printed Concrete: Influencing Factors and Method of Enhancing. In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 12, pp. 241–264.
31. Malaeb, Z.; AlSakka, F.; Hamzeh, F. 3D Concrete Printing: Machine Design, Mix Proportioning, and Mix Comparison between Difference Machine Setups. In *3D Concrete Printing Technology*, 1st ed.; Sanjayan, J.G., Nazari, A., Nematollahi, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; Volume 6, pp. 115–136.
32. BS 1881-116:1983. Available online: https://shop.bsigroup.com/ProductDetail/?pid=000000000000049171 (accessed on 10 July 2019).
33. Li, L.; Wang, R.; Lu, Q. Influence of Polymer Latex on the Setting Time, Mechanical Properties and Durability of Calcium Sulfoaluminate Cement Mortar. *Constr. Build. Mater.* **2018**, *169*, 911–922. [CrossRef]
34. Ohama, Y. *Study on Properties and Mix Proportioning of Polymer-Modified Mortars for Buildings*; Report of the Building Research Institute: Tsukuba-shi, Japan, 1973; p. 120. (In Japanese)
35. Ohama, Y. Recent Research and Development in Polymer-Modified Mortar and Concrete. In *Proceedings of the 3rd Beijing International Symposium on Cement and Concrete, Beijing, China, 27–30 October 1993*; Wu, Z.Q., Jiang, J.F., Huang, S.Y., Tong, S.D., Shen, R.X., Fu, Z.C., Xi, Y.Z., Eds.; International Academic Publishers: Wabernstrasse, Switzerland, 1993.
36. Hashimoto, H.; Ohama, Y. Strengths of Polymer-Modified Concrete. *Con. J.* **1977**, *15*, 117–124. (In Japanese)
37. Xu, F.; Peng, C.; Zhu, J.; Chen, J. Design and Evaluation of Polyester Fiber and SBR Latex Compound-Modified Perlite Mortar with Rubber Powder. *Constr. Build. Mater.* **2016**, *127*, 751–761. [CrossRef]
38. Yun, K.K.; Kim, D.H.; Kim, K.J. Effect of Micro Air Void System on the Permeability of Latex-Modified Concretes with Ordinary Portland and Very Early Strength Cements. *Can. J. Civ. Eng.* **2007**, *34*, 895–901. [CrossRef]
39. Bhogayata, A.C.; Arora, N.K. Workability, Strength, and Durability of Concrete Containing Recycled Plastic Fibers and Styrene-Butadiene Rubber Latex. *Constr. Build. Mater.* **2018**, *180*, 382–395. [CrossRef]
40. Kuhlmann, L.A. The Effect of Cure Time on Chloride Permeability of Latex-Modified Concrete. In Proceedings of the 1984 American Concrete Institute Fall Convention, New York, NY, USA, 27 October 1984; Ignacio Martin, American Concrete Institute: Farmington Hills, MI, USA, 1984.
41. Kuhlmann, L.A.; Foor, N.C. Chloride Permeability Versus Air Content of Latex Modified Concrete. *Cem. Con. Aggreg.* **1984**, *6*, 11–16. [CrossRef]
42. Beeldens, A.; Van Gemert, D.; Schorn, H.; Ohama, Y.; Czarnecki, L. Chloride Permeability Versus Air Content of Latex Modified Concrete. *Mater. Struct.* **2005**, *38*, 601–607. [CrossRef]