

Combined Effects of TiO₂ Nanoparticles and Waste Plastic Fiber to Enhance Mechanical Properties of Concrete Materials

Belete Balta¹, Dawit Gemechu (PhD)²

Addis Ababa Institute of Technology, School of Multidisciplinary Engineering,
Center of Materials Engineering, Ethiopia

beletebalta@gmail.com¹, dawitayana@gmail.com²

Abstract

This paper outlines experimental study on enhancing crack-resistance behavior of concrete materials by combined effects of TiO₂ Nanoparticles (TNPs) and Waste Plastic Fibers (WPFs). To enhance conventional concrete materials; cement was partially substituted with wt. % of (0, 0.5, 1.0, and 1.5) TNPs and sand partially substituted with WPFs by wt. % of (0, 0.2 and 0.4) for C-25 grade concrete. The properties of modified and unmodified concrete after 3, 7 and 28 days of curing time have been tested. The test results of combined effects of TNPs and WPFs indicated maximum enhancement in both mechanical and durability properties for all samples. The concrete properties have been tested via Scanning Electron Microscope (SEM), XRD (X-Ray Diffraction (XRD) and Differential Scanning Calorimetry – Thermo-Gravimetry analysis (DSC-TGA). The SEM tests results indicated the existence of Calcium Hydroxide (C-H) and Calcium-Silicate-Hydrate (C-S-H) components in the microstructure. The C-S-H compositions were responsible components for modifications of concrete properties. On the other hand, the XRD test results ensured the existence of extra-phases in the concrete structure. Moreover, the TGA analysis showed maximum weight loss has been realized in reduced temperatures for unmodified concrete than modified concrete. The DSC curve in the graphs exhibits crystallizations of different components during exothermic heating process. This paper has been conducted to indicate the combined effects of TNPs and WPFs have better effects in enhancing the cracks-resistance behavior than individual components in the concrete. The combined effects in advance solved concrete properties with respect to strength and quality, and serviceability rather than being creating opportunity of sustainability and eco-friendly concrete materials.

Keywords: Nanomaterials, TiO₂ nanoparticles, Cracks-Resistant Behavior, Mechanical Strength, C-S-H gel

Introduction

Concrete is commonly and widely used construction materials for building houses, dams, road infrastructures and etc. Conventional concrete materials (CCMs) have brittle behavior, and is susceptible to the spread of uncontrolled cracks and provide short service life (Ma, Li et al. 2015). Hence, ensuring the durability, and improving mechanical strength of building construction demands search for modern and innovative materials (Pietrzak, Adamus et al. 2016). Mankind have thirst for development of high-performance modern construction materials. However, developing high performance concrete materials involves consumptions of more cement, high content of aggregates and less water (Ceran, Şimşek et al. 2019), which is not cost effective in concrete industry. Recent reports showed that incorporations of limited amounts of nanoparticles is noticeable to improve mechanical and durability properties in concrete industry (Xu, Xi et al. 2018). Nanoparticles have ability in modifying concrete's mechanical and durability properties through providing high specific surface area, leading to acceleration of the hydration rate and filling of the pores in CCMs (Wu, Shi et al. 2016).

The characteristic features of nanoparticles enables to fill the voids and pores in concrete microstructure and produce denser concrete materials than CCMs (A and M 2017). The filling effects of nanoparticles results in inhibiting cracks initiation and growth at very early times and prevents crack propagation. The existence of nanoparticles in concrete composition helps to assure bond quality and integrity between cement paste and aggregates. The incorporation of nanoparticles could rapidly generate additional calcium silicate hydrate (C-S-H) gels, which is responsible for concrete materials microstructure enhancement. In concrete industry, compact microstructure and optimizing the composition of C-S-H gels is very critical issues to govern the durability (Wu, Shi et al. 2016). In addition to this, the incorporation of TiO₂ nanoparticles caused a reduction in the air pollution concentration of nearly 20 % (Pietrzak, Adamus et al. 2016), due to photocatalytic properties of TiO₂ nanoparticles.

Moreover, earlier reports indicated that waste plastic fiber or waste Polyethylene Terephthalate (PET) incorporated into concrete structures could improve the split tensile

strength, ductility and toughness of concrete materials (Foti 2011). PET bottles is highly disposed in everywhere, and has huge impacts in environmental pollution (Pereira, de Oliveira Junior et al. 2017). The partial replacement of fine aggregate with WPF was intended to save the depletion of virgin sand materials and keep away the shortage of river sand in the near future (Vishwakarma and Ramachandran 2018). Waste PET fibers achieved outstanding performance in terms of tensile, crack resistance and ductility (Alani, Bunnori et al. 2019) in concrete technology. *Another work by (Mustafa, Hanafi et al. 2019) revealed that the incorporation of WPF have significant effects on development of compressive strength. Furthermore, the incorporation of smaller particles, form a more compacted structure and then, improved the compressive strength of concrete (Ceran, Şimşek et al. 2019). The modification of compressive strength with nanoparticles is mostly due to the filling effects of nanoparticles (Diab, Elyamany et al. 2019).*

In this paper, it is aimed to enhance the crack-resistant behavior by partially substituting Cement with TiO_2 Nanoparticles (TNP) and Sand (fine aggregates) with Waste Plastic Fiber (WPF). The combined effects of these materials could be able to fill the voids in CCMs, and therefore, improved the mechanical and physical properties, through enhancing impermeability of water and other chemicals, that affect stability of concrete structures. Hence, the addition of TiO_2 nanoparticles and WPF enhances the density of concrete and its ability to withstand aggressive environmental conditions to ensure long service life.

Experimental Part

Materials and methods

For this experiment, locally available Ordinary Portland Cement (OPC) 42.5 R grade, which was manufactured by Dangote cement industry, was used. The anatase form of TNP (99.9 % of purity, with 5 nm scales, purchased from Sky-Spring Nano-materials, Inc. industry), was used. Ground waste PET bottles with particle size of 4.75 mm have been partially substituted fine aggregates with various proportions. Coarse and fine aggregates were purchased from its supplier found at (Addis Ababa, Ethiopia). The size of coarse aggregates were 19 mm, 9.5 mm and 4.75 mm and that of fine aggregates were (4.75, 2.36, 1.18) mm, (600, 300, and 150) μm . The Ethio-plast - 505 super-plasticizer as an admixture was obtained from GSM (Ethiopia), to assure well mixing of nanoparticles in water. Clean DI water was used for mixing and washing of concrete ingredients. To prepare CCMs; 505 super plasticizers, has been firstly mixed in water

and then, separately prepared components, like coarse aggregates, fine aggregates, and cement were mixed uniformly in a concrete blender, and then, the mixture of water and super plasticizers have been poured into concrete blender and stirred for 5 minutes. For the modified concrete materials; that contain both TNP and WPF; 505 super plasticizers, has been firstly mixed with water in a mixing bath, and then, TNP has been added and stirred at a high speed for 5 minutes. The raw ingredients, such as coarse and fine aggregates, ground waste PET bottles and cement were mixed in a concrete blender, and then after, the mixture of water, 505 super plasticizers and TNP have been slowly poured into concrete blender, and automatically stirred for about 7 minutes to achieved proper workability. Finally, the fresh concrete has been poured into oiled molds to form concrete samples. Then, an external vibrator is used to enable concrete compaction and lessening the amount of air bubbles. The specimens were demolded after 24 hours and then, cured in a water bath in material test lab and finally dried at a room temperature. Table 1 shows mix design of the prepared concrete samples. The experimental mix design to prepare concrete materials by partially substituting cement with TNP with wt. % of (0 %, 0.5 %, 1 % and 1.5 %) and fine aggregates with WPF with wt. % of (0 %, 0.2 % and 0.4 %) found in the table 1 below. Table 1: Mix design of the prepared concrete sample

Sample name	TNP wt %	WPF wt %	Cement kg/m ³	TNP kg/m ³	Water kg/m ³	FA, kg/m ³	CA, kg/m ³	WP kg/m ³	505 SP (ml)
CCMs	0	0	364.62	0.00	196.9	948.56	1097.3	0.00	10.00
TNP0.5	0.5		362.79	1.84	196.9	948.56	1097.3	0.00	10.00
TNP1	1		360.98	3.64	196.9	948.56	1097.3	0.00	10.00
TNP1.5	1.5		359.14	5.48	196.9	948.56	1097.3	0.00	10.00
TNP0.5+WPF0.2	0.5	0.2	362.79	1.84	196.9	946.67	1097.3	1.896	10.00
TNP0.5+WPF0.4	0.5	0.4	362.79	1.84	196.9	944.77	1097.3	3.79	10.00

Characterization

Field emission scanning electron microscope (FE-SEM) was used to investigate the morphology of the synthesized concrete samples. The FE-SEM analysis were performed on unmodified, 1.0 % TNP modified and (0.5 % TNP + 0.4 % WPF) modified concrete samples. Inspect F-50 FE-SEM American model for general purpose machine at an accelerating voltage of 10.00 kV was used.

The X-ray diffraction technique is employed here to analyze the structural characteristics of the unmodified and modified concrete samples. The x-ray spectra of the samples were recorded in the 2θ range of $10 - 80^\circ$ at continuous scan mode with a scan speed of $4^\circ/\text{min}$. The analysis was conducted at 40 kV and 30 mA with a $\text{CuK}\alpha$ radiation ($\lambda=0.154 \text{ nm}$).

The thermal behavior of the unmodified and modified samples has been studied by differential scanning calorimetry and thermogravimetric analysis (TGA). An instrument (SDT Q600 V20.9 Build 20) was used for thermal analysis. Alumina powders were used as a reference. The heat treatment was carried under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ from 20°C to 800°C .

Results and Discussion

The compressive strength test has been conducted on unmodified and modified samples, according to the ASTM C-109. Accordingly, all the modified concrete samples showed better compressive strength compared to unmodified samples (Table 2). However, maximum compressive strength was achieved for (0.5TNP + 0.4WPF) sample, i.e. 39.05 MPa. TNP is expected to accelerate the hydration reactions, mainly of the reaction between C_3S & C_2S with water, since they are the major components and their reaction in turn generates additional C-S-H gels, which is responsible for the improvement of the concrete strength. Further, the combined effects of TiO_2 nanoparticles and WPFs, has improved the bond strength and integrity between cement paste and aggregates in concrete mix.

Table 2: Compressive strength (MPa), Splitting Tensile Strength (MPa), Load Resistance (KN/mm^2) and weight loss (g) of the samples after 3, 7 & 28 days of curing time

Sample Name	Compressive strength (MPa)			Splitting Tensile strength (MPa)			Load Resistance KN/mm^2			Permeability Test: Wight loss (g)
	Curing time (3, 7, and 28 days)									
	3	7	28	3	7	28	3	7	28	28
CCM	17.3	22.06	29.01	3.98	4.89	5.14	0.39	0.50	0.65	134
TNP0.5+WPF0.2	23.59	29.60	37.50	4.76	6.02	6.18	0.53	0.67	0.84	89
TNP0.5+WPF0.4	31.57	34.28	39.05	5.74	7.42	9.52	0.71	0.77	0.87	70
TNP0.5	27.95	29.79	34.29	4.58	5.73	7.29	0.63	0.67	0.77	82
TNP1	29.53	30.76	36.86	5.06	5.82	7.42	0.69	0.71	0.87	76
TNP1.5	28.96	28.32	30.66	4.94	5.78	6.80	0.63	0.64	0.70	88

The split tensile strength test was also performed on all samples and the results were reported on (Table 2). The split tensile strength after 3 days of curing time for unmodified concrete showed 3.98 MPa, while the concrete modified with (0.5 % TNP + 0.2 % WPF) showed 4.76 MPa. The concrete modified with both (0.5 % TNP + 0.4% WPF), showed 5.74MPa. The concrete modified with (0.5 % TNP + 0.4 % WPF) showed 7.42 MPa for the sample cured for 7 days, whereas the split tensile strength value increased to 9.52 MPa for the sample cured for 28 days. It is also important to note that the split tensile strength slightly reduced when the TNP was increased from 1 % to 1.5 % TNP, possibly due to agglomeration effects of TiO_2 nanoparticles. The existence of TNP facilitated the hydration reaction between C_3S and C_2S and provided opportunity to create cement hydration products. On the other hand, WPF incorporation has improved the prevention of crack initiation and propagation, and has played bridging effects in macro and micro cracking, restrained and delayed crack growth rate within concrete structure.

Furthermore, the maximum load resistance of 0.87 KN/mm^2 was obtained for the (TNP0.5+WPF0.4) sample as reported in (table 2). Incorporation of TNP was expected to form a more compacted and homogeneous structure in the concrete samples. Also, the waste plastic fibers have improved toughness and fracture resistance of concrete structure.

Percentages of water absorption have been recorded to evaluate the water permeability. A reduction in the percentage of water absorption by reducing the total pore volume within a concrete structure was observed. As shown in (Table 2), the combined effects of TiO_2 nanoparticles and waste plastic fibers led to an increased degree of hydration and integrity between concrete components that resulted in decrease water permeability. TNPs have accelerated the hydration reaction and have converted calcium hydroxide to calcium silicate hydrates, and hence this component has filled pores to prevent water penetrations. The TNP played nucleation effects, while WPF blocked the pores and, the water absorption has dramatically reduced. However, the increased contents of TiO_2 nanoparticles negatively affected concrete strength due to the agglomeration effects. The high surface area of the TiO_2 nanoparticles and the blocking effects of WPF could be main mechanisms for modification.

FE--SEM micrographs of unmodified, and modified samples were reported in fig 1 (a, b and c). FE-SEM image of unmodified (CCM) sample shown in Figure 1(a) reveals that it is observed that the sample contains largely of unhydrated products, which are calcium hydroxide. The existence of brighter region indicated the formation of calcium hydroxides in the compositions.

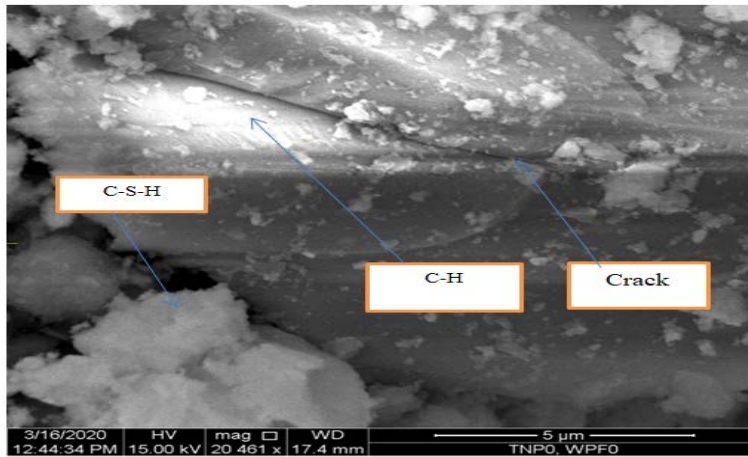


Figure 1 (a): SEM micrographs of unmodified (CCM) sample

Fig. 1 (b) shows FE-SEM image of (0.5% TNP + 0.4 % WPF). The image showed a large amount of gel like materials existence, which is C-S-H that is responsible to fill the pores in the concrete microstructures to enhance the concrete properties. Uniformly dispersed TiO_2 nanoparticles accelerated the formations of C-S-H components in the whole concrete structure by controlling the crystallization process and hence, restricted the growth of $\text{Ca}(\text{OH})_2$. TiO_2 nanoparticle serves as the nuclei, which will change the hydration process, and thus, leading to the morphology change of the hydration products. Furthermore, it could be able to fill the nano-sized pores in the amorphous cementitious hydration products to reduce permeability of aggressive environmental conditions, and tend to increase density C-S-H phase.

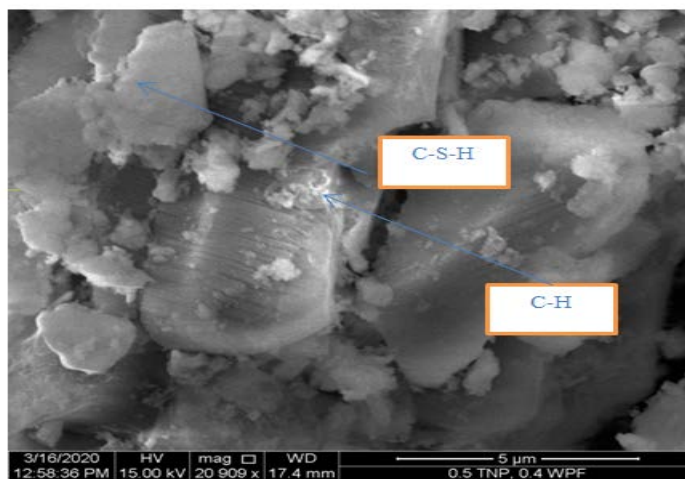


Figure 1 b: SEM micrograph of 0.5 % TNP + 0.4 % WPF modified sample

FE-SEM micrograph of 1 % TNP modified concrete shown in Figure 1 (c) indicated large amount of gel like material, which is C-S-H generated. At the same time, crystallization of concrete components is very limited. The partial replacement of cement with TNP accelerated

the hydration process in concrete, and helped to generate more C-S-H gel like material, which is responsible for improving durability and mechanical properties.

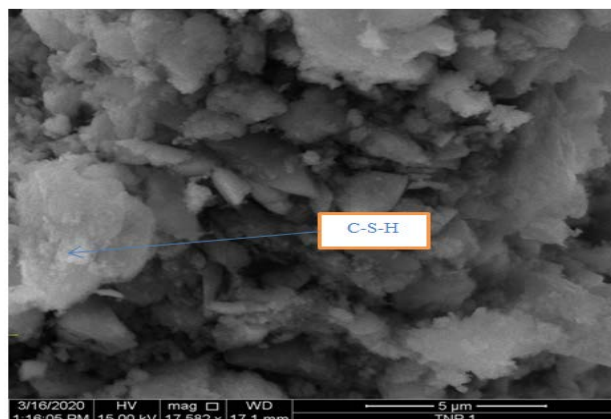


Figure 1 (c): SEM micrograph of 1% TNP modified concrete

Figure 2 shows the XRD results for the CCM and concrete modified with TiO_2 nanoparticles and waste plastic fiber. In case of CCM, the samples have shown unhydrated C-H phases at ($2\theta = 10.90^\circ$, 29.44° , and 29.46°). However, these phases were suppressed (absent) for the modified (1% TNP and 0.5% TNP and 0.4% WPF) samples. Furthermore, the CCM samples have the unhydrated C_3S and C_2S phases at ($2\theta = 26.72^\circ$) and ($2\theta = 28.76^\circ$), respectively. In case of TiO_2 nanoparticles modified samples, the hydrated C-S-H phases appeared at ($2\theta = 47.14^\circ$ and 50.26°) and the C-H phases that appeared in CCM sample at ($2\theta = 10.90^\circ$) was possibly converted into C-S-H phase in both (0.5% TNP & 0.4% WPF) and (1% TNP) samples.

The SiO_2 (quartz) compositions peaks appeared for all the diffractograms at ($2\theta = 18.17^\circ$, 29.91° , and 31.18°). The modifications of concrete materials with the partial replacement of cement with TNP and sand with WPF, ensured with the increase in the peak corresponding to C-S-H phases, and simultaneously reduction in the C-H, C_3S and C_2S phases. This could be attributed due to the enabling of hydration reactions in the cement paste, and the consumption of $(\text{CaOH})_2$, C_2S and C_3S to form an extra C-S-H gels like material.

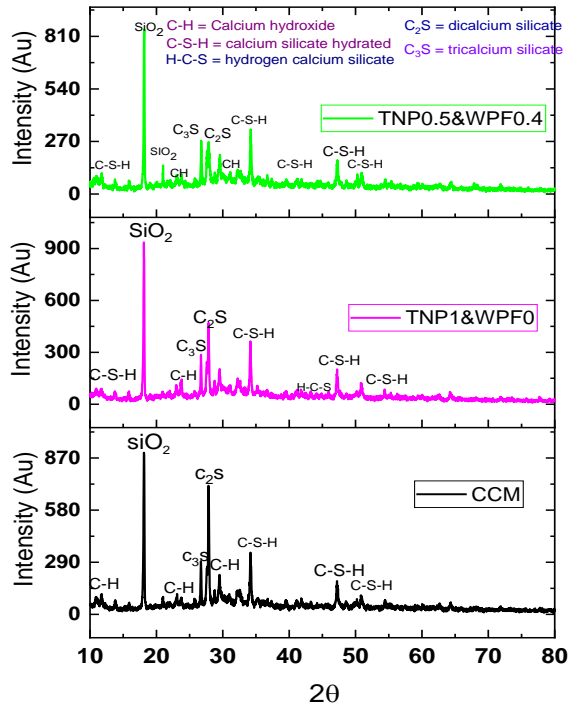


Figure 2: XRD spectra of unmodified (CCM), and modified with 1% TNP and (0.5% TNP & 0.4% WPF) modified samples

(Figure 3), the thermo-gravimetric tests were also done to find the thermal stability of concrete materials. The TGA-DSC tests were conducted starting from room temperature to 800°C temperature ranges with increasing heating rate of 10°C/minute. The weight loss has been appeared up to about 100 °C was due to dehydration and moisture removal from the sample. The maximum weight loss has recorded at the temperature of 426.43 °C and 433.85 °C for CCM; and TNP and WFP modified samples due to dehydroxylation and other hydration products, respectively. The mass loss occurred at about 668°C was attributed to the decarbonation of calcite (CaCO_3) in cement paste.

The DSC plot exhibited three main exothermic events during the entire heating process. The first occurs on the temperatures range from the onset to 77 °C for the unmodified sample, and at 82 °C for the modified samples. These weight losses were resulted from the dehydration and evaporation of moisture contents. Similarly, for modified concrete, (fig 3.6b), exhibits three main exothermic events. The first exothermic reaction occurred from onset temperature to 106 °C. At 106 °C, heat is absorbed - endothermic transition. From 106 °C to 380 °C, crystallization occurred - an exothermic event. Finally, bond formations occurred. At temperature of 380 °C again melting take place. Furthermore, from 380 °C to 600 °C crystallization undertakes.

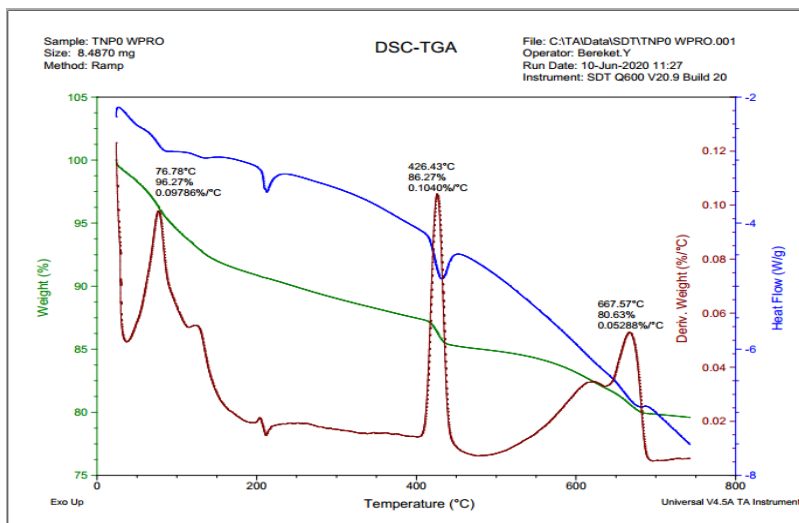


Figure 3a: DSC-TGA result of unmodified concrete materials

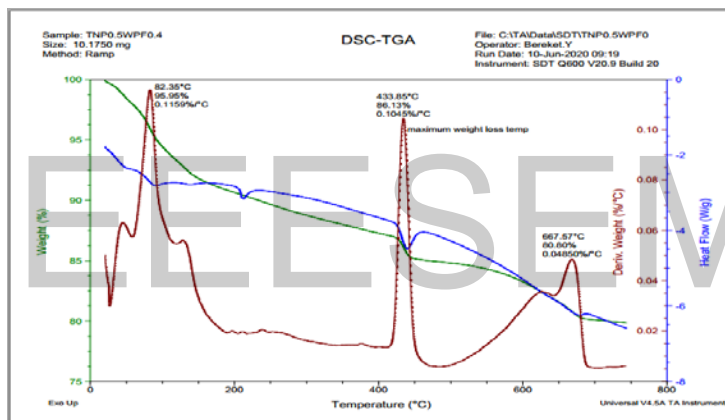


Figure 3 b: DSC-TGA results of 0.5 % TNP & 0.4 % WPF modified concrete

Conclusions

In this paper, the combined effects of TiO_2 nanoparticles and waste plastic fiber with various compositions were investigated. The results from mechanical tests indicated that both TiO_2 nanoparticles and waste plastics fibers have improved the mechanical properties like compressive strength, splitting tensile strength and maximum load resistance of the concrete materials. In addition, all of the modified concrete showed enhanced properties with respect to water permeability. In particular, 0.5 % TNP + 0.4 % WFP sample showed remarkable improvement in all aspects. For instance, the compressive strength of both TiO_2 nanoparticles and waste plastic fibers modified concrete after 28 days of curing time showed 29.01 to 39.05 MPa. Similarly, the split tensile strength showed increment from 5.14 to 9.52 MPa.

From the morphological study; the microstructure of modified concrete showed well-formed gels like materials, this is the indication of the existence of C-S-H. The thermal analysis of modified concrete indicated weight loss appeared at relatively higher temperatures than unmodified concrete sample. Furthermore, the XRD test result of unmodified concrete has shown the existence of various unhydrated phases like C-H, C₂S, C₃S and other unhydrated phases. Contrarily, the presence of hydrated phases, such as C-S-H gel like phases have confirmed modification in concrete materials. In general, the concrete materials modified with TiO₂ nanoparticles and waste plastics fiber has clearly shown developed cracks-resistance behavior in concrete structure.

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References

1. A, V. and S. M (2017). "Usage of Carbon nanotubes and nano fibers in cement and concrete: A review." *International Journal of Engineering and Technology* 9(2): 564-569
2. Alani, A. H., et al. (2019). "Durability performance of a novel ultra-high-performance PET green concrete (UHPPGC)." *Construction and Building Materials* 209: 395-405.
3. Bhogayata, A. C. and N. K. Arora (2018). "Workability, strength, and durability of concrete containing recycled plastic fibers and styrene-butadiene rubber latex." *Construction and Building Materials* 180: 382-395.

4. Ceran, Ö. B., et al. (2019). "Effects of dispersed and powdered silver nanoparticles on the mechanical, thermal, electrical and durability properties of cementitious composites." *Construction and Building Materials* 222: 152-167.
5. Diab, A. M., et al. (2019). "Effect of nanomaterials additives on performance of concrete resistance against magnesium sulfate and acids." *Construction and Building Materials* 210: 210-231.
6. Foti, D. (2011). "Preliminary analysis of concrete reinforced with waste bottles PET fibers." *Construction and Building Materials* 25(4): 1906-1915.
7. Han, Wang et al. (2017). "Properties and modification mechanism of nano-zirconia filled reactive powder concrete" 426-434
8. Harilal, M., et al. (2019). "High performance green concrete (HPGC) with improved strength and chloride ion penetration resistance by synergistic action of fly ash, nanoparticles and corrosion inhibitor." *Construction and Building Materials* 198: 299-312.
9. Ma, Li et al. (2015). "Effects of Nano-TiO₂ on the Toughness and Durability of Cement-Based Material." *Advances in Materials Science and Engineering* 2015: 1-10.
10. Mustafa, M. A.-T., et al. (2019). "Effect of partial replacement of sand by plastic waste on impact resistance of concrete: experiment and simulation." *Structures* 20: 519-526.
11. Paul, S. C., et al. (2018). "Properties of cement-based composites using nanoparticles: A comprehensive review." *Construction and Building Materials* 189: 1019-1034.
12. Pereira, E. L., et al. (2017). "Optimization of mechanical properties in concrete reinforced with fibers from solid urban wastes (PET bottles) for the production of ecological concrete." *Construction and Building Materials* 149: 837-848.
13. Pietrzak, A., et al. (2016). "Application of Titanium Dioxide in Cement and Concrete Technology." *Key Engineering Materials* 687: 243-249.
14. Vishwakarma, V. and D. Ramachandran (2018). "Green Concrete mix using solid waste and nanoparticles as alternatives – A review." *Construction and Building Materials* 162: 96-103.
15. Wu, Z., et al. (2016). "Effects of different nanomaterials on hardening and performance of ultra-high strength concrete (UHSC)." *Cement and Concrete Composites* 70: 24-34.
16. Xu, Xie., et al. (2018). "Environmental resistance of cement concrete modified with low dosage nano particles." *Construction and Building Materials* 164: 535-553.