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Effect of Using Nano-TiO_2 on the Rheological Properties of Cementitious Systems

Hatice Gizem Sahin
Bursa Uludag University

Fatih Eren Akgumus
Bursa Uludag University

Ali Mardani
Bursa Uludag University

Abstract: Self-cleaning concrete (SCC) was developed that can reduce air pollution by utilizing its photocatalytic property. Due to this feature, polluting materials are broken down into H_2O and CO_2, which are completely harmless, without the need for any additional carrier gas. For this purpose, it was emphasized that semiconductor oxides with photocatalytic properties such as TiO_2, ZnO, CdSe and WO_3 are used in the production of SCC. Compared to other oxides, it was determined that nano-TiO_2 is more commonly preferred. However, it was emphasized that the use of nano-TiO_2 due to the high surface area/volume ratio increases the water requirement and the risk of agglomeration of cementitious systems. This situation directly affects the rheological properties of SCC. In this study, the effects of nano-TiO_2 utilization ratio change on the rheological properties of cementitious systems were investigated. For this purpose, a total of 4 mixtures were prepared by substituting nano-TiO_2 with 28 nm at a rate of 0, 0.5, 1 and 1.5% by weight of cement. The rheological properties of the prepared mixtures were evaluated according to the dynamic yield stress (DYS), apparent viscosity (AV) and structural build-up (A_{thix}) parameters. It was understood that the DYS, AV and A_{thix} values of the mixtures increased with the increase of nano-TiO_2 utilization ratio.

Keywords: Self-cleaning concrete, nano-TiO_2, Rheological properties, Structural build-up

Introduction

As urbanization becomes more widespread, it was understood that environmental pollution has significantly increased, leading to a decrease in air quality (Mardani-Aghabaglou, 2016; Sezer et al., 2016; Yigit et al., 2020; Mardani-Aghabaglou et al., 2018). The fact that these issues stem from numerous parameters was emphasized. It was observed that a significant number of studies related to the reduction of pollutants within the framework of the European Green Deal are currently underway. In a study conducted by Nath et al. (2016), the presence and quantity of volatile organic compounds such as C, N, and S oxides resulting from industrialization were emphasized as directly affecting air quality. In this context, it was emphasized that issues such as global warming, pollution risk, acid rain, and changes in concrete surface color have increased, while human health was significantly adversely affected (Beeldens, 2006). Several methods were implemented to mitigate these adversities.

In this study, the color change of concrete surfaces due to pollutants was examined. In this regard, it was understood that the application of photocatalysis, which accelerates the natural degradation process, holds the potential to be a solution to this problem (Yang et al., 2000). The use of photocatalysts in cementitious systems was observed to preserve the aesthetic properties of concrete, purify it from pollutants, and maintain the same color and texture (Visali et al., 2021). It was emphasized that semiconductors are the most suitable photocatalysts due to their photocorrosion resistance and wide bandgap energies (Castro Hoyos et al., 2022; Liang et al., 2019).

It was reported that TiO_2, due to its low cost, non-toxic nature, and good thermal stability, is the most commonly used semiconductor photocatalyst (Yuranova et al., 2007; Yasmina et al., 2014). There were sufficient studies on the impact of TiO_2 (nT) usage on the self-cleaning and mechanical properties of concrete mixtures (Wang et al., 2019). However, it was found that there is a lack of information in the literature regarding the impact of nT usage on the rheological properties and thixotropic behavior of cementitious systems (Li et al., 2020). Observations have revealed that in a limited number of conducted studies, conflicting results were reported. Various researchers have noted that the use of nano-materials, which increases the risk of agglomeration due to their high surface area, directly affects the flow performance of cementitious systems (Song et al., 2021; Mohseni et al., 2015; Temel et al., 2023). It was understood that this situation necessitates the determination of rheological properties that provide information about the homogeneity and workability of cementitious systems containing nT (Talero et al., 2017).

Many researchers have reported that the increase in the use of nano-materials and their usage rate in cementitious systems generally has a negative impact on their rheological properties (Nazar et al., 2020). However, it was determined that a definitive conclusion on this matter has not been reached in mixtures containing nT. This study investigates the impact of the usage rate of nT on the rheological properties and thixotropic behavior of cement paste mixtures.

Materials and Methods

CEM I 42.5 Portland cement was used as the binder. The chemical components provided by the manufacturer, along with some of the physical and mechanical properties of the used cement, are presented in Table 1.

Table 1. Some properties of the cement.

Oxides (%)						
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O+0,658 K_2O	SO_3
18	4.75	3.58	63	1.4	0.7	3.11
Specific Gravity	Surface Area (cm^2/g)	Compressive Strength (MPa)		Setting Time (minutes)		
		7-Day	28-Day	Initial	Final	
3.06	3441	42.8	51.8	170	240	

Table 2 displays a few of the nT's properties that were supplied by the manufacturer.

Table 2. Some properties of the used nT in the study

Value	Units	28 nm NT
Purity	%	>99
Size	nm	28
Specific Surface Area	m^2/g	>60
Loss of Weight in Drying	%	2 max.
Loss of Weight in Ignition	%	5 max.
pH	-	5.5-7.0
Color	-	White

A water reducing admixture (WRA) was used to achieve the desired flow performance. Some characteristics of the WRA provided by the manufacturer, are shown in Table 3.

Table 3. Some properties of WRA

Density (g/cm^3)	Solid Content (%)	pH	Chlorine content (%)	Na_2O ratio (%)
1.060	32	2-5	<0.1	<10

Preparation of Mixtures

In addition to the control, a total of four different paste mixtures were prepared by adding nT at a rate of 0.5%, 1%, and 1.5% by weight of the cement. In order to achieve the desired flow performance, WRA was added to all mixtures at a rate of 0.15% by weight of the binder. The selection of these ratios took into account the measurement capacity of the rheometer used and the prevention of segregation in the mixtures. The mixture ratios are shown in Table 4. The nT utilization ratio was used for the nomenclature of the mixtures. For example, the mixture containing 1.5% nT is named 1.5-nT.

Table 4. Amounts of prepared mixtures

Mixture	Cement	nT	w/b	WRA (%)
C	1	-	0.35	0.15
0.5-nT	0.95	0.5		
1.0-nT	0.90	1		
1.5-nT	0.85	1.5		

Method

The rheological parameters of the paste mixtures were measured, including the DYS and AV values. Furthermore, the thixotropic behavior of the mixtures was examined by calculating the structural build-up development (A_{thix}).

Determination of Rheological Properties

For rheological measurements, an MCR52-Anton Paar rheometer with an 8 mm ball was used, as shown in Figure 1-a. The rheological measurement method applied in the study is depicted in Figure 1-b.

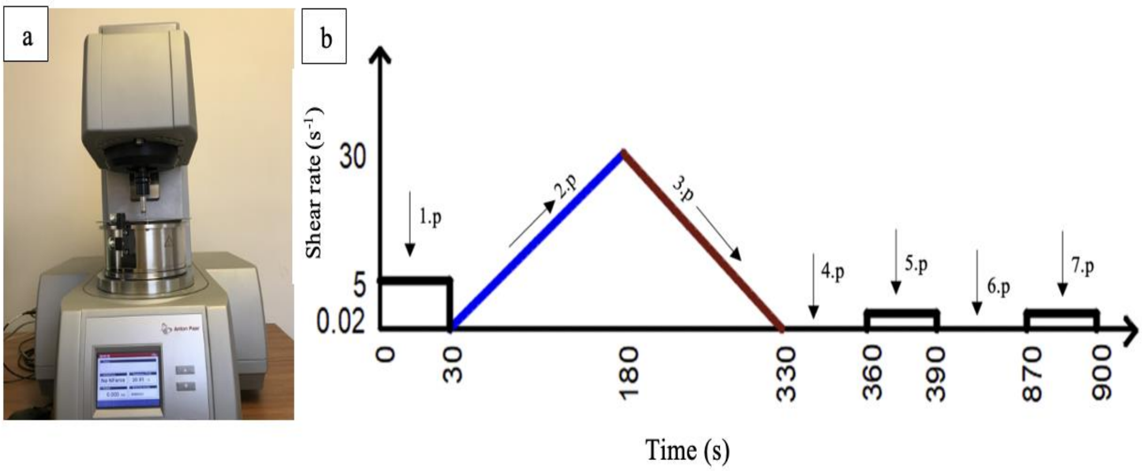


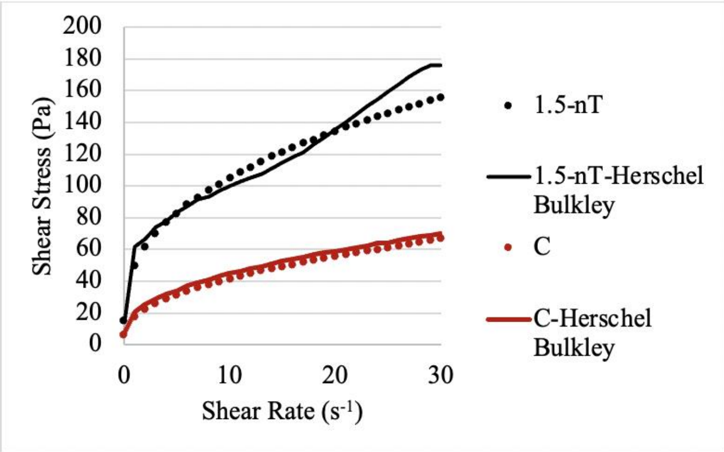
Figure 1. (a) Rheometer and (b) rheological measurement system

In order to determine the rheological measurements, shear stress-shear rate and AV-shear rate graphs were obtained for each mixture, considering the data obtained in the 3rd period as shown in Figure 1-b. The Herschel-Bulkley model was used in the analysis of rheological data.

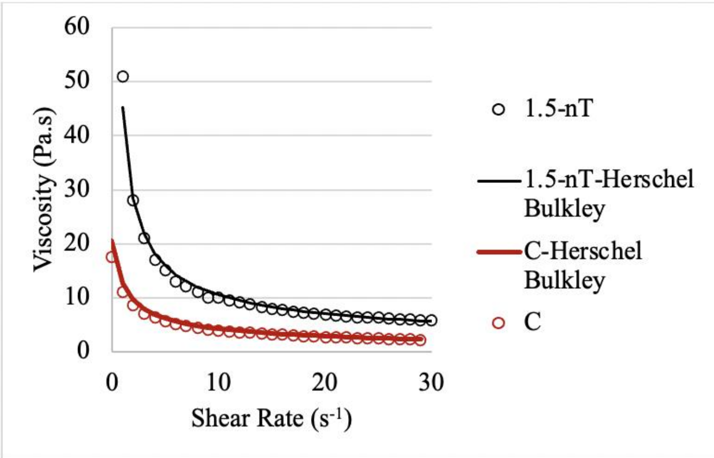
The shear stress/AV-shear rate graph for the C and 1.5-nT mixtures is shown in Figure 2.

Measurement of Thixotropic Behavior

Using the static yield stress values obtained from this test, the structural build-up development (A_{thix}) of the mixture was determined (Sahin & Mardani, 2022).



(a)



(b)

Figure 2. (a) DYS-shear rate and (b) AV-shear rate for the 1.5-nT mixtures

Results and Discussion

Rheological properties and thixotropic values are shown in Table 5. The addition of nT to paste mixtures generally rises their rheological properties and thixotropic values, regardless of the utilization ratio. The rise in the total surface area due to the addition of nT was reported by various researchers to lead to an rised risk of agglomeration, thus potentially negatively affecting the flow performance of cementitious systems (Nazari et al., 2012; Wiesner et al., 2017). It was emphasized by many researchers that in the system, as the content of fine materials rises and the total surface area rises, the water requirement of the mixture also rises (Mardani-Aghabaglou et al., 2017; Senff et al., 2014). Furthermore, various researchers have emphasized that nT can accelerate the formation of nuclei in the matrix, potentially rising the hydration rate and, consequently, leading to a rise in heat of hydration (Lee et al., 2013; Zhang et al., 2015). In this case, various researchers have expressed that the rise in the amount of evaporating water may negatively affect the rheological properties of the mixtures (Yang et al., 2023; Sun et al., 2020).

With a rise in the nT utilization ratio from 0.5% to 1.5%, the DYS, AV, and A_{thix} values of the mixture rised by 76%, 133%, and 60%, respectively. De Matos et al. (2022) reported that in 3D-printed concrete mixtures containing nT at 0.25, 0.50, 0.75, 1, and 1.5% ratios, a rise in the nT utilization ratio had a negative impact on the rheological properties of the mixtures. It was reported that this phenomenon is due to the high surface area of nT and its reduction of the interparticle spacing (Bergold et al., 2013). However, in another study conducted by Jiang et al. (2018), it was measured that an rise in the nT utilizatiоn ratio resulted in a decrease in the AV value of the mixtures. This phenomenon is due to the lubricating and ball-bearing role of spherical particles between the cement flocculation structures.

Table 5. Rheological and thixotropic values of mixtures

Mixture	DYS (Pa)	AV (Pa.s)	A_{thix} (Pa/s)
C	7.8	2.3	0.04
0.5-nT	8.7	2.4	0.05
1.0-nT	10.3	2.6	0.07
1.5-nT	15.3	5.6	0.08

Conclusion

The results obtained from the materials used and the experiments conducted are listed below:

- Regardless of the utilization ratio, the addition of nT generally resulted in a rise in the rheological properties and thixotropic values of the paste mixtures.

- A rise in the nT utilization ratio was observed to enhance the rheological properties of cement paste mixtures and improve their structural build-up behavior.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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Author Information

Hatice Gizem Sahin
Bursa Uludag University, Faculty of Engineering,
Department of Civil Engineering, Nilufer/Bursa/Turkey

Fatih Eren Akgumus
Bursa Uludag University, Faculty of Engineering,
Department of Civil Engineering, Nilüfer/Bursa/Turkey

Ali Mardani
Bursa Uludag University, Faculty of Engineering,
Department of Civil Engineering, Nilufer/Bursa/Turkey
Contact e-mail: ali.mardani16@gmail.com

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