Nigerian Journal of Technology (NIJOTECH)
Vol. 41, No. 3, May, 2022, pp.438-443
www.nijotech.com

Print ISSN: 0331-8443
Electronic ISSN: 2467-8821
http://dx.doi.org/10.4314/njt.v41i3.3

Assessment of Crystallite Phase, Morphology and Mechanical Properties of Concrete reinforced with Polyethylene Terephthalate (PET)/Carbon Nanotubes (CNTs)

A. S. Hussaini[1], J. O. Tijani[2], M. A. T. Suleiman[3], A. S. Abdulkareem[4], S. Mustapha[5, *], M. M. Ndamitso[6]

[1,2,5,6]*Department of Chemistry, Federal University of Technology, PMB, 65, Minna, Niger State, NIGERIA.*
[2,4]*Department of Chemical Engineering, Federal University of Technology, PMB. 65, Minna, Niger State, NIGERIA.*
[2,3,4,5]*Nano.Research Group, Africa Center of Excellence for Mycotoxin and Food Safety, Federal Uni. of Tech., Minna, Niger State, NIGERIA.*

Abstract
PET (Polyethylene terephthalate) is a semicrystalline thermoplastic polymer with good chemical resistance, thermal stability, melt mobility, and spinnability. In recent years, the development of nanocomposites with various types of nanomaterials has become a fascinating topic in material science. The polyethylene terephthalate (PET) blended with carbon nanotubes (CNTs) was mixed with concrete to prepare concrete/PET/CNTs nanocomposites. The PET/CNTs were employed as reinforcing material to study the synergistic effect between PET/CNTs and concrete. The impact of PET/CNTs at different ratios on the crystallite phase and morphology of the materials was examined using X-ray diffraction spectroscopy (XRD) and high-resolution scanning electron microscopy (HRSEM), respectively. The mechanical properties were tested using tensile, compression, and flexural measurement. The presence of PET/CNTs changes the orientation of minerals, thus reducing the crystallite sizes in the matrices at a higher amount of PET/CNT. The excellent mechanical strength of the composite materials gradually increased with the increase in concrete/PET/CNTs. The concrete/PET/CNT (1:4) performance was far from rutting due to the excellent compatibility and crosslinking between the reinforcing material and the concrete, thus increasing the mechanical strength and improving the resistance to cracking.

Keywords: Polyethylene terephthalate, carbon nanotubes, crystallites sizes, and mechanical properties.

1.0 INTRODUCTION

Plastic waste is given considerable attention nowadays because it emphasizes non-biodegradable behavior (Adeyanju *et al*., 2021). Plastic wastes thus exert a more significant impact on the environment (Moharir and Kumar, 2019). In developing countries such as Nigeria, the main process of waste disposal is considered a big challenge (Taiwo, 2009). This has resulted in large quantities of garbage in landfills that are not reduced due to trash removal from the environment (Lee *et al*., 2006). Consequently, the need to open new disposal increased from time to time. Polyethylene terephthalate (PET) is usually used for plastic bottles of carbonated drinks and mineral water (Welle and Franz, 2011; Koshti *et al*., 2018).

Waste plastic bottles are also readily available due to the high consumption rates compared with other categories of plastic (Bošnir *et al*., 2007). The bottles are often not colored and have a high light penetration rate compared to other plastics (Evans and Hensley, 2004).

Nowadays, plastic usage has become an integral part of our lives (Subramanian, 2000). There are many waste plastic bottles found in Nigeria and in any developing country in the world today (Kehinde et al., 2020). Therefore, the amount of waste plastic bottles is very high, and it has become a problem for the environment and humans (Aurah, 2013). Thus, the plastic bottles cannot be disposed of by dumping or burning, as they release poisonous fumes, produce uncontrolled fire or contaminate the soil and vegetation (Trivedi *et al*., 2020).

Also, this situation has created a big problem for the environment due to the inability to accommodate the increasing number of plastic wastes (Zhang *et al.*, 2010). One of the methods to reduce the amount of waste plastic bottles is to use them as an ingredient in concrete mixes to

*****Corresponding author (**Tel:** +234 (0) 7039651120)

Email addresses: saidua@yahoo.com (Hussaini, A. S.), *jimohtijani@futminna.edu.ng* (Tijani, J. O.), *smatsule@yahoo.com* (Suleiman, M. A. T), *kasaka2003@futminna.edu.ng* (Abdulkareem, A. S.), *saheedmustapha09@gmail.com* (Mustapha, S.), *muhd.ndamitso@futminna.edu.ng* (Ndamitso, M. M.)

improve the quality of concrete (Nibudey *et al.,* 2013; Hake *et al*., 2020).

Recently, nanomodification of concrete has shown outstanding potential in increasing the performance of the pavement. Researchers have studied the modifications of concrete with nanomaterials such as ZnO, TiO_2, clay, and CNTs to enhance concrete materials' durability and mechanical properties. Among various nanomaterials, CNTs known for their electrical, excellent, and thermal properties are promising modifiers for mixtures. CNTs can be synthesized using different methods. However, this study considered the vapour deposition method due to its simplicity and production of high-quality CNTs at controlled temperature and pressure. For instance, Hassanzadeh-Aghdam *et al.* (2019) reported that CNTs/steel fiber reinforced concrete improved the thermal conductivities, and the agglomeration of CNTs led to a reduction in the concrete thermal conductivities, thus causing interfacial thermal resistance weakness. This study provides an alternative method for managing the environmental conversion of plastic waste to a more helpful material (Dinda, 2004). In addition, this study is also expected to promote the use of leftovers like plastic bottles in the construction industry to help control pollution to the environment (Luhar and Luhar, 2019). The main objective of this research is to study the effect of the addition of waste plastic bottles modified with CNTs in concrete. XRD was performed to determine the change in the crystalline phase of the concrete/PET/CNTs. Subsequently, the mechanical strength of concrete/CNTs/CNTs was determined.

2.0 MATERIALS AND METHODS

2.1 Materials

The cement used in this study was Dangote Cement, produced at Obajana, Kogi State. This cement conforms with ASTM150-92, BS&EN197-1:2000, SON. The Minna-based, well-graded natural silica sand was sourced from a river off Eastern Bye-pass, Minna, Niger State. Its grading conformed to the SON standard. The gravel with a maximum size of 19 mm used in this study was obtained in Minna. Polyethylene terephthalate (PET) wastes were obtained from Bosso Campus, FUT Minna, Niger State, Nigeria. Multi-walled carbon nanotubes (MWCNTs) were produced on a $CaCO_3$-supported bimetallic (Fe-Co/$CaCO_3$) catalyst via a catalytic vapour deposition (CVD) technique.

2.2 Methods

2.2.1 Mixing procedure

The material, a combination of cement, sand, and gravel at a ratio of 1:2:4, respectively, was mixed by a mechanical mixer of 0.1 m^3 capacity, then the modified PET/CNTs were added by sprinkling during mixing. Modified PET/CNTs were added as a percentage by volume, and compacting of specimens was done by a vibrator machine.

PET was shredded and heated in an oven until melted, then CNTs were slowly added to the molten sample in a percentage ratio of 1:1 to obtain PET/CNTs modified. The speed of the mixer was kept at 500 rpm at 150 °C. The different volume fractions adopted were 0%, 0.1%, 0.2%, 0.5% and 1% (by volume).

This research was designed to study the effect of adding modified PET/CNTs on concrete's compressive, tensile, and flexural strength. 0%, 0.1%, 0.2%, 0.5%, and 1% modified PET/CNTs content were used to evaluate the influence of modified PET/CNTs on the compressive, tensile, and flexural strength of concrete. For the compressive and splitting tensile strength test, fifteen cubes specimens (150 x 150 x 150) mm and cylinders specimens (100x200) mm were tested at 28 days. Also, a third point loading test was used to examine twelve 100 x 100 x 400 mm prisms with three reference prisms to evaluate the influence of modified PET/CNTs on the flexural strength of concrete.

2.2.2 Mechanical properties

Cube specimens with 150 x 150 x 150 mm dimensions were cast for the compressive strength test. The molds were filled with 0%, 0.1%, 0.2%, 0.5% and 1% modified PET/CNTs. The vibration was given to the moulds using a table vibrator. The top surface of the specimen was levelled and finished. After 24 hours, the specimens were demoulded and then transferred to a curing tank, wherein they were allowed to cure for 28 days. After 28 days of curing, these cubes were tested on a digital compression testing machine as per I.S. 516-1959. The failure load was noted.

The cylinder specimens of dimensions 100 x 200 mm were cast to determine splitting tensile strength. The moulds were filled with 0%, 0.1%, 0.2%, 0.5% and 1% modified PET/CNTs. In each category, three cubes were tested and their average value. Third point loading test to examine twelve 100 x100 x400 mm prisms with three reference prisms to evaluate the influence of modified PET/CNTs on the flexural strength of concrete.

2.2.3 Production of carbon nanotubes

The Fe-Co/$CaCO_3$ catalyst (1 g) was weighed into a boat and placed horizontally in a tubular quartz reactor in a furnace (CCVD). The furnace was heated at 10 °C/min while argon (carrier gas) flowed over the catalyst at 30 cm^3/min for 90 minutes before the reaction temperature was reached. The synthesized CNTs were treated with a concentrated HNO_3 and H_2SO_4 mixture (v/v 1:3) to remove carbonaceous and metallic impurities present in the carbon materials. The mixture was then ultrasonicated for 3 h at 40 °C to introduce the oxygen group to the surface of the treated CNTs. The oxidized CNTs were cooled at room temperature and mixed with 300 cm^3 of cold deionized water. The mixture was then filtered through a PTFE 0.22 µm filter. The residue was thoroughly rinsed with deionized water until the pH became neutral and was afterward oven-dried at 80 ^{0}C for 8 h.

3.0 RESULTS AND DISCUSSION

3.1 XRD result of concrete and PET/CNTs modified

The XRD patterns of the concrete incorporating PET are presented in Fig. 1 and 2. Minerals such as calcite, calcium silicate, gypsum, quartz, and calcium magnesium aluminium iron silicate were identified in the samples. In Fig. 1, the samples exhibit a significant change in the orientation of minerals when compared to Fig. 2. The typical amorphous calcium silicate was present in the XRD patterns of concrete/PET/CNTs at 1:1, 1:2. 1:3 and 1:4 in Fig. 1, while the presence of pronounced calcite in Fig. 2 could be due to incorporating more concrete in the matrices. The diffraction peaks of XRD patterns at 2θ = 18.32° and 22.80° signify calcium silicate and calcite, respectively, in the samples, as depicted in Fig. 2. The XRD peaks at 2θ = 18.32°, 22.80°, and 29.21° correspond to calcite in the concrete mixing ratio in

Fig. 2. It can be deduced that an increase in concrete in the matrices brings about a replacement of calcium silicate with calcite (see Fig. 2). Generally, no formation of a new phase other than the minerals mentioned earlier for both concrete matrices. Although, there are some differences in the intensities of the minerals in the XRD patterns of the matrices. The crystallite sizes of the predominant mineral, calcite in concrete/PET/CNTs at 1:1, 2:1, 3:1, and 4:1 are 29.26 nm, 29.90 nm, 31.28 nm, and 32.70 nm, respectively, while the crystallite sizes of concrete/PET/CNTs at 1:1, 1:2, 1:3 and 1:4 are 26.10 nm, 24.34 nm, 19.50 nm, and 18.60 nm, respectively. The reduction in crystallite sizes in the matrices at a higher amount of PET/CNTs may be attributed to the chain-like structure of CNTs to PET polymer molecular chains. This could further be explained by the nucleation effect between the CNTs and the composite, which contributes to the interfacial adhesion matrix.

In Fig. 1 and 2, the XRD results reveal the presence of calcium silicate, calcite, quartz, and gypsum. The calcium silicate was low in the concrete mixture at a high ratio with PET/CNTs (Fig. 2). This shows a synergy between the reaction of calcium silicate and PET/CNTs in the compounding ratios of a higher amount of cement to the polymer.

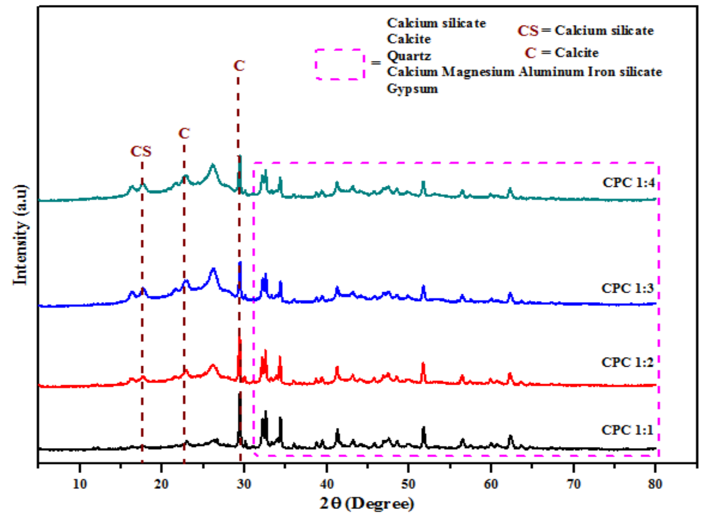

Figure 1: *XRD results of concrete and PET modified CNTs at (a) 1:1 (b) 1:2 (c) 1:3 (d) 1:4*

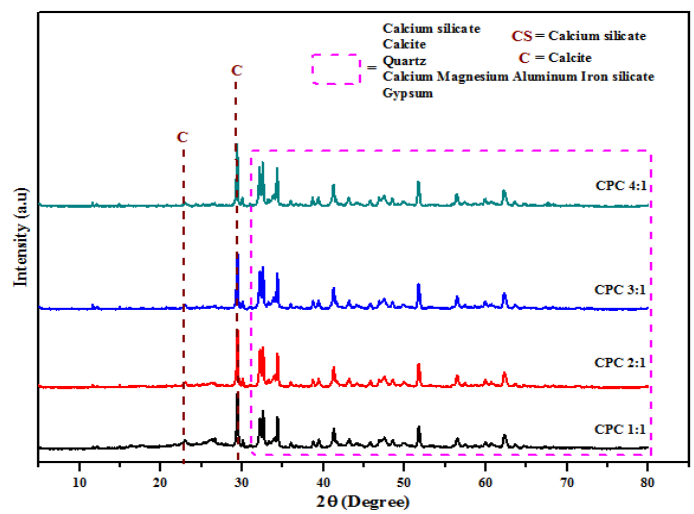

Figure 2: *XRD results of concrete and PET modified CNTs at (a) 1:1 (b) 2:1 (c) 3:1 (d) 4:1*

3.2 HRSEM pattern of concrete and PET modified CNTs

Fig. 3 and 4 show that concrete accumulates in PET/CNTs composites. CNTs have a similar chain-like structure to PET molecular chains for all samples. The nucleation effect occurs among the CNTs, concrete, and PET particles, thus contributing to interfacial adhesion in the matrix. In Fig. 4, the composites contained a high amount of PET/CNTs, and it was observed that the higher the concrete in the matrices, the higher the spherical phase of asphalt. A more homogeneous phase morphology occurred in the composites. This illustrates an apparent interfacial adhesion between the concrete and PET/CNTs.
Furthermore, the PET/CNTs distribution in asphalt is not intensive, as depicted in Fig. 3 and 4. The excellent bonding between concrete and PET/CNTs was observed in

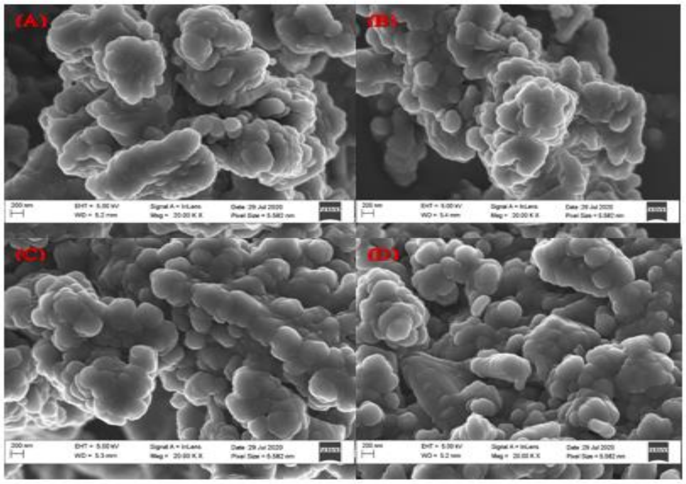

Fig. 3: *HRSEM pattern of concrete and PET modified CNTs at (A) 1:1 (B) 1:2 (C) 1:3 and (D) 1:4*

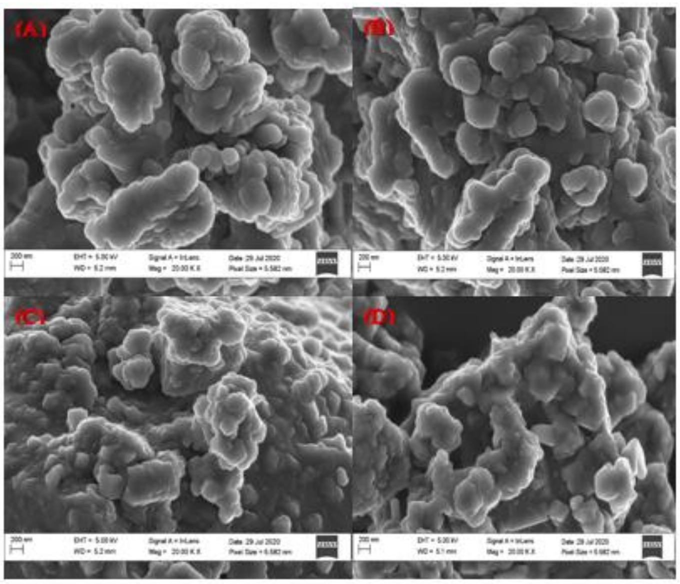

Figure 4: *HRSEM pattern of concrete and PET modified CNTs at (A) 1:1 (B) 2:1 (C) 3:1 and (D) 4:1*

all the composites. However, no aggregation morphology was formed, and the PET/CNTs in the matrices exhibited homogeneous dispersion. The accumulation of concrete in the matrices becomes intense; therefore, the mechanical characteristic of composites likely reduces or increases. The non-appearance of CNTs in the morphological patterns may be attributed to the formation of clusters and bonding between CNTs and cement, making it not very effective because of the lack of uniform dispersion (Sanjeev *et al.*, 2015). No cracks were observed in all the composites. This implies that PET/CNTs could serve as an excellent anti-aging agent for the performance of concrete matrices. It was established in this study that PET/CNTs modified in concrete showed higher penetration degree and good dispersion of PET/CNTs, and their elemental composition is presented in Tables 1 and 2.

Table 1: Elemental composition of concrete and PET modified CNTs at (A) 1:1 (B) 1:2 (C) 1:3 and (D) 1:4

Element	A	B	C	D
O	59.97	43.67	60.91	35.62
Mg	1.33	1.42	1.38	1.33
Al	2.45	1.56	2.60	2.16
Si	6.98	8.43	7.67	8.13
S	0.35	0.59	0.75	1.06
Ca	27.46	42.56	25.39	49.82
Fe	1.46	1.40	1.01	1.88

Table 2: Elemental composition of cement and PET modified CNTs at (A) 1:1 (B) 2:1 (C) 3:1 and (D) 4:1

Element	A	B	C	D
C	-	-	23.57	42.21
O	59.97	55.28	33.21	39.66
Mg	1.33	-	0.73	0.54
Al	2.45	0.52	1.46	1.00
Si	6.98	1.89	5.91	3.25
P	-	-	0.24	0.09
S	0.35	17.31	0.96	0.26
Ca	27.46	25.01	32.43	12.52
Fe	1.46	-	1.52	0.46

3.3 Mechanical properties

The mechanical properties of PET/CNTs modified concrete is presented as presented in Fig. 5 show the improvement of mechanical properties of concrete due to adding different percentages of modified PET/CNTs, especially the flexural strength, from 2.210 MPa for reference mix to 16.348 MPa for 1 % modified PET/CNTs. For compressive strength tests, the improvement was also good. The reference mix shows that the compressive strength was 23.7 MPa, and this value was improved to 48.36 MPa for 1% modified PET/CNTs mixes, and tensile strength was improved from 2.456 to 5.126 MPa. The figures show increased compressive, tensile, and flexural strength, respectively. The main explanation for the improvement in those properties was a result of enhancement of the formation of stronger bonds between the modified PET/CNTs on the bond between concrete ingredients (Singh *et al*., 2020). The mechanical properties of the modified PET/CNTs have a very high tensile strength of about 2850 MPa, which improves the mechanical. Table 3 shows the mineral composition of concrete with modified PET/CNTs used in this study.

Table 3: Mechanical properties of concrete modified PET/CNTs at different ratios

PET/CNTs ratio %	0	0.1	0.2	0.5	1
ACS of 3 cubes (MPa)	23.73	30.58	33.25	38.45	48.36
ASTS of 3 cubes (MPa)	2.456	3.236	3.326	4.189	5.126
AFS of 3 cubes (MPa)	2.210	6.137	7.938	11.597	16.348

Keys: ACS = Axial compression specimen, ASTS = Automatic surface to surface, AFS = American Foundry Society

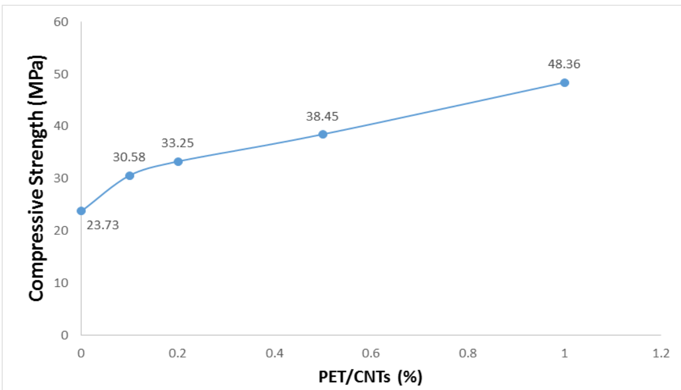

Figure 5: *Increasing compressive strength with various PET/CNTs ratios.*

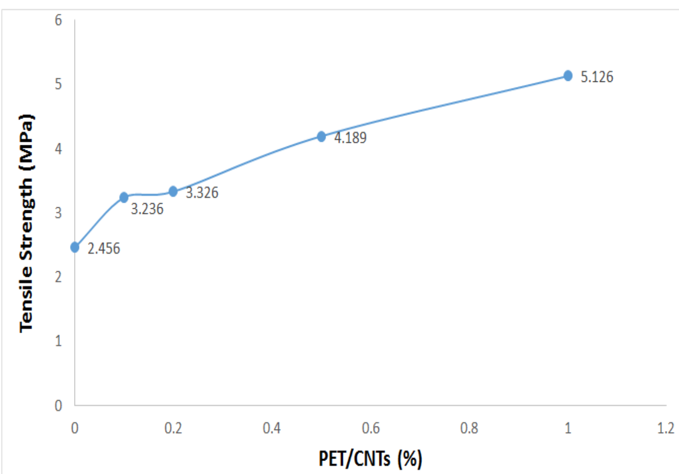

Figure 6: *Increasing tensile strength with various PET/CNTs ratios.*

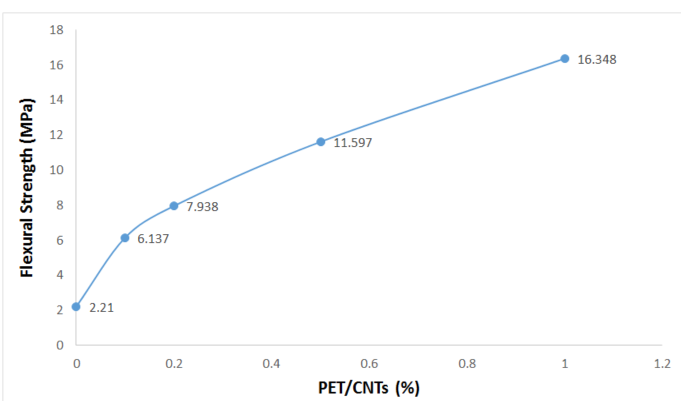

Figure 7: Increasing flexural strength with various PET/CNTs ratios.

4.0 CONCLUSION

This work conducts experimental research on the crystalline phase, and mechanical properties of PET/CNTs modified concrete mix at different ratios. The crystallite phase of the modified concrete was identified via XRD analysis, which shows changes in crystalline phases. The influence of modified PET/CNTs on concrete's compressive, tensile and flexural strength was studied within different modified PET/CNTs ratios. The higher the percentage of modified PET/CNTs in the concrete mix, the higher the strength of the composite. It reveals that as modified PET/CNTs increase, the development of strength increases compared with the control mixture.

Similarly, improvement in the development of flexural strength in concrete with added 0.1 %, 0.2 %, 0.5 %, and 1% of modified PET/CNTs was observed in this study. It can be concluded that concrete with added modified PET/CNTs ratios is excellent. The addition of modified PET/CNTs in concrete mixes would appear to be more reliable and help resolve some solid waste problems, preventing environmental pollution and assuring sustainable development.

REFERENCES

[1] Adeyanju, G. C., Augustine, T. M., Volkmann, S., Oyebamiji, U. A., Ran, S., Osobajo, O. A., Otitoju, A. "Effectiveness of intervention on behaviour change against the use of non-biodegradable plastic bags: a systematic review", *Discover sustainability*, *2*(1), 2021, pp. 1-15.

[2] Aurah, C. M. "Assessment of the extent to which plastic bag waste management methods used in Nairobi City promote sustainability", *American Journal of Environmental Protection*, *1*(4), 2013, pp. 96-101.

[3] Bošnir, J., Puntarić, D., Galić, A., Škes, I., Dijanić, T., Klarić, M., Šmit, Z. "Migration of phthalates from plastic containers into soft drinks and mineral water" *Food Technology and Biotechnology*, *45*(1), 2007, pp. 91-95.

[4] Dinda, S. "Environmental Kuznets curve hypothesis: a survey", *Ecological economics*, *49*(4), 2004, pp. 431-455.

[5] Evans, M. R., Hensley, D. L. "Plant growth in plastic, peat, and processed poultry feather fiber growing containers", *HortScience*, *39*(5), 2004, pp. 1012-1014.

[6] Hake, S. L., Damgir, R. M., Awsarmal, P. R. "Utilization of plastic waste in bitumen mixes for flexible pavement", *Transportation Research Procedia*, *48*, 2020, pp. 3779-3785.

[7] Hassanzadeh-Aghdam, M. K., Mahmoodi, M. J., Safi, M. "Effect of adding carbon nanotubes on the thermal conductivity of steel fiber-reinforced concrete. *Composites Part B: Engineering*, 106972, 2019.

[8] Kehinde, O., Ramonu, O. J., Babaremu, K. O., Justin, L. D. "Plastic wastes: environmental hazard and instrument for wealth creation in Nigeria" *Heliyon*, *6*(10), 2020, 05131.

[9] Koshti, R., Mehta, L., Samarth, N. "Biological recycling of polyethylene terephthalate: a mini-review. *Journal of Polymers and the Environment*, *26*(8), 2018, pp. 3520-3529.

[10] Lee, S., Xu, Q., Booth, M., Townsend, T. G., Chadik, P., Bitton, G. "Reduced sulfur compounds in gas from construction and demolition debris landfills", *Waste management*, *26*(5), 2006, pp. 526-533.

[11] Luhar, S., Luhar, I. "Potential application of E-wastes in construction industry: A review", *Construction and Building Materials*, *203*, 2019, pp. 222-240.

[12] Moharir, R. V., Kumar, S. 'Challenges associated with plastic waste disposal and allied microbial routes for its effective degradation: a comprehensive review", *Journal of Cleaner Production*, *208*, 2019, pp. 65-76.

[13] Nibudey, R. N., Nagarnaik, P. B., Parbat, D. K., Pande, A. M. "Strength and fracture properties of post consumed waste plastic fiber reinforced concrete", *International Journal of Civil, Structural, Environmental and Infrastructure Engineering Research and Development (IJCSEIERD)*, *3*(2), 2013, pp. 9-16.

[14] Singh, A. K., Bedi, R., Kaith, B. S. "Mechanical properties of composite materials based on waste plastic–A review", *Materials Today: Proceedings*, *26*, 2020, pp. 1293-1301.

[15] Subramanian, P. M. "Plastics recycling and waste management in the US", *Resources, Conservation and Recycling*, *28*(3-4), 2000, pp. 253-263.

[16] Taiwo, A. "Waste management towards sustainable development in Nigeria: A case study of Lagos State", *International NGO Journal*, *4*(4), 2009, pp. 173-179.

[17] Trivedi, M., Mathur, M., Johri, P., Singh, A., Tiwari, R. K. "Waste management: A paradigm shift In Environmental concerns and sustainable development, *Springer*, 2020, pp. 337-363.

[18] Welle, F., Franz, R. "Migration of antimony from PET bottles into beverages: determination of the activation energy of diffusion and migration modelling compared with literature data" *Food Additives & Contaminants: Part A*, *28*(1), 2011, pp. 115-126.

[19] Zhang, D. Q., Tan, S. K., Gersberg, R. M. "Municipal solid waste management in China: status, problems and challenges" *Journal of environmental management*, *91*(8), 2010, pp. 1623-1633.