



Chemical Depolymerization of Waste PET Bottles in Bubble Column Reactor for Sustainable and Thermal Installation of Cement Mortar Composites



Mohammed Alzuhairi,* Sarmad Imad Ibrahim, Amjed M. Hameed

Department of materials engineering, University of Technology, Baghdad, Iraq

Abstract

Plastic is one of the most frequently utilized materials on the world. At the same time, most of this plastic will turn into waste. The recycling processes are not enough, and creating new uses for this plastic waste is an optimum solution. The current research utilized a three-phase bubble column reactor in the PET depolymerization process. Depolymerized PET (DPET) powder was utilized for replacing sand with four different percentages of DPET of 1, 3, 6, and 9% to improve several physical characteristics of cement mortar composites. According to the results, the use of a three-phase bubble column reactor in the depolymerization of waste PET reduced the processing time to less than one hour. The thermal conductivity and the density of the mortar decreased when replacing the sand with DPET powder. This effect rises with an increase in the DPET content. The results also demonstrate that the mortar with 9% DPET particles was 15.45 percent lighter than that without DPET particles. The thermal conductivity of the mortar with 9% DPET was 18.27 percent lower than the mortar without DPET particles.

"Keywords: Depolymerization; PET; thermal conductivity; density; porosity; mortar."

1. Introduction

Human beings consistently produce trash and dispose of it differently, so solid waste management can be considered one of the oldest issues. The amounts and types of the produced waste, disposal approaches, and human values and perceptions of what needs to be done with that waste have changed. However, owing to the ease of production and low pricing, the uses of plastics and their composites continue to increase fast. This rapid growth is why high amounts of plastic waste accumulate, creating considerable challenges for their disposals [1-3].

Despite plastic's suitability for many different applications, organizations face a growing issue about finding alternative approaches for disposing of massive amounts of waste packaging. Plastic waste disposal in the environment has been considered one of the big problems because of its low biodegradability and presence in significant chemicals [4-6].

The thermal insulation of the cement mortar composites, is one of the important factors, this is because it is an indicator of the amount of heat lost

while passing through the mortar. The heat loss amount via the roofs and the walls have directly affected the constructions' energy consumption. The temperature, moisture content, cementations material type, aggregate type, and concrete density have been considered influential aspects of thermal conductivity. The building's heat transfer and energy consumption are reduced when the mortar has a low thermal conductivity value (k-value); in other words, the mortar has high thermal insulation [7, 8].

Real et al. indicated that the heating energy in the European countries might be decreased by 15% with the use of the structurally lightweight aggregate concrete compared to standard concrete. The lightweight aggregate concrete has presented itself as one of the alternatives to the traditional weight concrete. Its thermal features and the reduction of thermal bridging impacts keep building energy requires maintaining the levels of the thermal comfort in the buildings [9, 10].

Mortar thermal conductivity decreases when the substitution level of the plastic waste aggregate (PWA) increases. Sand's thermal conductivity is

*Corresponding author e-mail: mohammed.a.alzuhairi@uotechnology.edu.iq;

Receive Date: 03 February 2022, Revise Date: 23 March 2022, Accept Date: 14 April 2022, First Publish Date: 14 April 2022
DOI: 10.21608/EJCHEM.2022.119943.5382

©2022 National Information and Documentation Center (NIDOC)

higher in comparison to that of the PWA. The PWA slows the thermal heat transfer down [11].

Meyer et al., [12] have utilized the radial heat flow approach to evaluate the thermal conductivity for the mortar containing the sand's PWA replacement. Thermal conductivity has been reduced by 13%, 31%, and 66% for the mortars that contain "10%, 20%, and 50%" PWA. The researchers have attributed such reduction to PWA's low thermal conductivity compared to the natural sand.

Ferandiz et al., [13] have utilized the "TT-TC Probe Thermtest Inc." device to determine the thermal conductivity for a mortar that has 2 PWA forms fine aggregate substitution. The first form is a ground PWA, passing through a 1mm sieve with $0.013\text{g}\cdot\text{cm}^{-3}$ density, whereas the other form is a powdered PWA passed through a 0.5mm sieve with $0.022\text{g}\cdot\text{cm}^{-3}$. Compared to traditional mortars, the k values were dropped by 60.5% for the ground PWA and 47.5% for the powdered PWA. Based on the authors' statement, the mortars containing the powdered PWA had lower thermal insulation than the ground PWA due to a higher level of bulk density. The process of powdering the PWA reduces trapped air in the mortar, identified as one of the powder form features. On the other hand, in the case of the ground PWA, the air is entrapped in the mortar, which describes the lower thermal conductivity.

Zaleska et al., [14] investigated the thermal conductivity of mortar containing PWA using the Isomet2114 device. The thermal conductivity has been decreased fast with increasing the PWA content. A thermal conductivity drops up to 86.4% at 50.6% PWA compared to the standard mortar. It was indicated that the increase of thermal insulating abilities of the mortar that contains the PWA to lower thermal conductivity of the PWA compared to the silica sand and the higher open porosity of the mortar with a higher amount of the PWA.

The classic depolymerization process of PET took a long time, reach to 8hrs. One of the methods used to improve the depolymerization process is using a bubble column reactor. The bubble column reactor contains a cylindrical container at the bottom division, and there is a gas inlet gate and gas distributor. There are liquid-liquid and liquid-solid phases. Using bubble column reactors in the depolymerization process of PET provides some benefits such as high heat transfer rate and decreased the time of the process, which means saving power and less cost [15-18].

In this study, the depolymerization process has been used for the PET waste pieces rather than used

these pieces directly in mortar. Using depolymerized PET (DPET) as a modifier in cement mortar composites might lessen the mismatch between sand and plastic materials observed when the latter is employed directly in mortar. This mismatch is the cause of mortar mechanical characteristics loss. It also decreases cement mortar composites' density and thermal conductivity while maintaining or reducing their porosity.

2. Materials and Experimental Procedure

2.1. Materials

The wastewater bottles were collected from the landfill and waste. PET was made from these bottles with high chemical resistance and a 26°C melting point [19, 20]. The wastewater bottles were cleaned and washed, and the labels were also removed. The bottles were cut into 2.5 mm square pieces, as demonstrated in Figure 1.

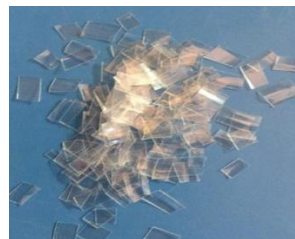


Figure 1. Waste PET Pieces

The fine aggregates (sand) that used in this work were named (Al-ikhaidher) available in the local market in Iraq. It has less than 4.7 mm grains particles size and a $1.674\text{ g}\cdot\text{cm}^{-3}$ density. Other properties are 0.5%, absorption coefficient, $1.69\text{ W}\cdot\text{m}\cdot\text{K}$ thermal conductivity, 2.63 fineness modulus, and 0.08% sulfate. The grading of sand is shown in Table 1.

Table 1. Sand Grading.

Size of The Sieve (mm)	% Passing, wt.
9.5	100
4.75	92.5
2.36	84.7
1.18	70.3
0.6	47.1
0.3	18.8
0.15	5.2

The cement applied in this investigation was ordinary portland cement (OPC) type II supplied by

the Al-Sulaimaniya factory in north Iraq. Its compressive strength was 31.7 MPa at 28 days. The density of the cement used was 1.435 g/cm³, and its fineness measured with the Blaine method was 2813 cm²/g. The time required for the first and final settings was 151 and 268 minutes, respectively. Table 2 presents the chemical content of the cement.

Table 2. Cement's Chemical Compositions.

Chemical Composition	Weight Percentage
Fe ₂ O ₃	3.71
SiO ₂	20.14
CaO	61.59
Al ₂ O ₃	5.24
SO ₃	1.83
MgO	1.96

2.2. Production of DPET Powder

The process of producing the DPET powder is by the depolymerized PET (100g) via a bubble column reactor with ethylene glycol (100mL) as solvent and Nano-MgO (0.01g) as a catalyst in 197°C. PET is depolymerized into monomers, dimers, trimers, oligomers, and other chemical components during the glycolysis process[21]. The Nitrogen gas inter to the reactor from the gate in the bottom and then pass from the distributor (ceramic filter set inside the cylinder) to the mix of PET pieces (solid phase) and EG (liquid phase), as seen in Figure 2. The pressure of the inlet nitrogen gas was fixed at 1 bar.

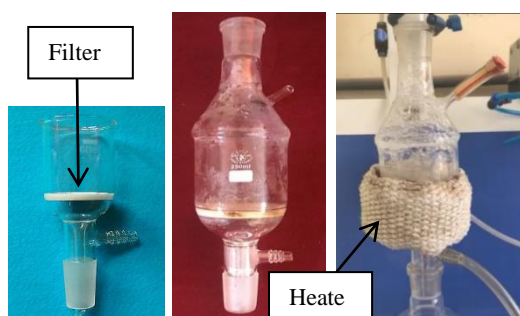


Figure 2. The Bubble Column Reactor.

A heater sited around the reactor was used to heat the PET to 197°C, as seen in Figure 2. The PET pieces and EG became one homogenous mixture that is completely depolymerized in each other in one liquid phase. The process takes less than one hour. As soon

as the gas stops entering the reactor, the hot homogenous liquid starts dropping in the collector beaker sitting bottom of the reactor. After a few minutes, this liquid was cooled and frizzed at room temperature, as seen in Figure 3.



Figure 3. The PET and EG became one homogenous mixture, frizzed at RT.

A physical separation process was carried out to the mixture To get rid of depolymerized PET (DPET) from the EG via exploiting the difference in evaporation temperatures.

As a result, the EG starts evaporating at 197°C before the DPET. 90% of the EG can take back using a horizontal condenser, as illustrated in Figure 4.



Figure 4. Separation EG from DPET process.

The remaining hot liquid in the beaker is poured into a flat plate to cool and dry at room temperature to form a homogenous layer that is crushed and milled to product powder. The powder was washed by distilled water to remove any remaining EG or Nano-MgO, and then filtered and milled to get a white powder, as shown in Figure 5.



Figure 5. The product after milling (DPET powder).

2.3. The Mixtures Design and Samples Preparation

The DPET replaced the fine aggregates in cement mortar in four different percentages. The standard cement mortar was considered as a reference mixture. The cement-to-water and sand-to-cement ratios were kept constant.

The mixing and sample preparation followed the ASTM C305-12. The mortar cement samples were poured into a mold and covered for one day. Following that, the specimens are pulled out and cured in a water bath. The samples were submerged in water for 28 days.

Table 3. The Mixture Details.

Groups	DPET wt%	Sand wt%	Cement wt%	(W/C) %	(S/C) %
MDPET0	0	100	100	0.480	2.75:1
MDPET1	1	99	100	0.480	2.75:1
MDPET3	3	97	100	0.480	2.75:1
MDPET6	6	94	100	0.480	2.75:1
MDPET9	9	91	100	0.480	2.75:1

2.4. The Test of Samples

The samples were kept in an oven at 105 to 115°C to remove the moisture [22]. The density of mortar was calculated according to ASTM C5677-14a. In contrast, the porosity of mortar was calculated according to ASTM C642. The thermal conductivity was recorded at room temperature according to ASTM C-1113 using the "QTM-500 device" (see Figure 6). All tests were done in the National Center for Construction Laboratories (NCCLR).



Figure 6. The Thermal Conductivity Test

2.5. DPET Characterization:

DPET powder was characterized in the National Center for Construction Laboratories (NCCLR) and University of Technology laboratories. The properties of DPET particles are tabulated in Table 4.

Table 4. DPET Properties.

Thermal Conductivity	(0.13 – 0.23) W/m. K.
Density	1.36 g/cm ³
Water Absorption	0%
Melting Point	258 C°
Chemical Resistance	High
The Color	White
Average particles size	5micron

The FTIR test of DPET particles is shown in Figure 7. The sharp peak at 1713.72cm⁻¹ is associated with "C=O" stretching band that represents the ester functional group. The peaks at 1409.55cm⁻¹ and 1341.56cm⁻¹ are attributed to the deformation (-C-H alkane). The sharp peak at 1246.55cm⁻¹ indicates the asymmetric "C-C-O" stretching results of the presence of carbon in the aromatic ring. The 871.46cm⁻¹ peak refers to aromatic C-H out of the plane. The sharp peak at 722.69cm⁻¹ is associated with aromatic C-H wagging. The FTIR analysis of DPET was nearly in agreement with Alzuhairi et al., [19]

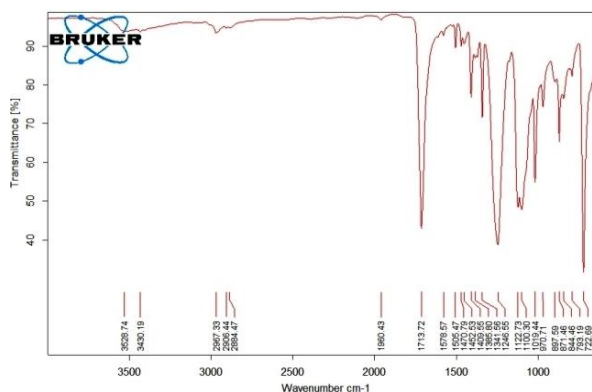


Figure 7. FTIR Spectroscopy of DPET.

3. Results and Discussion

3.1. Density Test

The densities of five mortar groups are shown in Figure 8. The results reveal that the mortar densities with DPET are lower than the mortar mixture without DPET (reference mortar), and the density decreases as DPET percentages increase.

This decrease is due to the fact that DPET particles have a density of 1.36 g/cm³ lower than that of the sand

particles (1.684 g/cm^3). These findings agree with those of Choi et al., [23]. The sand replacement with DPET in the mortar made lighter mortar. This substitution has a big impact at MDPET9 because the DPET amount was 9%, while it had a less effect at MDPET1 since the DPET amount was 1%. The findings also show that the MDPET9 mortar was lighter than the MDPET0 mortar by 15.45%.

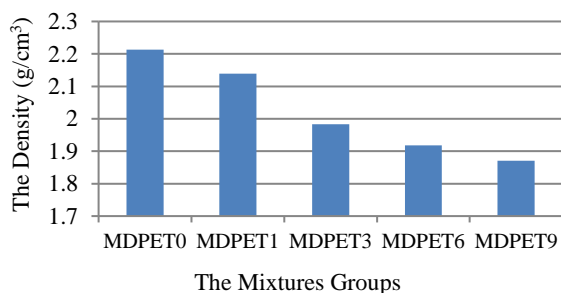


Figure 8. Impact of DPET content on mortar's density.

3.2. The Thermal Conductivity

Figure 9 illustrates the results of the thermal conductivity. The results of the thermal conductivity test showed that the mortar samples with DPET have thermal conductivities lower than the reference mortar. The thermal conductivity decreases as DPET percentages increase. These findings agree with those of both Ferrandiz et al., [13] and Zaleska et al., [14]. This behavior is because DPET particles have thermal conductivity 0.13 to 1.23 W/m.K lower than the thermal conductivity of sand particles, which is 1.69 W/m.K . The DPET particles cause slow heat flow drop in the cement mortar. Thus, the sand replacement with DPET in the mortar causes an increase in the thermal insulation properties of the mortar. The replacement impact is more obvious in MDPET9 mortar because the DPET quantity was 9%, but it is less evident in MDPET1 mortar because the DPET amount was 1%.

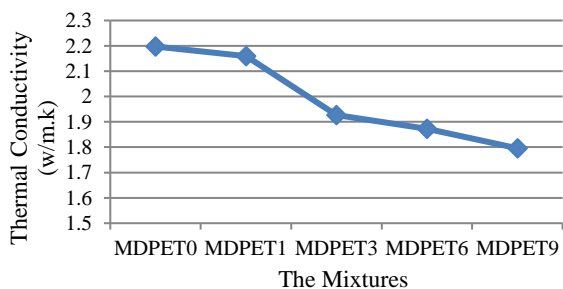


Figure 9. Impact of DPET content on mortar's thermal Conductivity.

3.3. Porosity

The mortar porosity of the mortar samples is shown in Figure 10. The findings of the mortar porosity test showed that the mortar mixtures with DPET have porosity lower than the reference mortar. The porosity decreased as DPET percentages increased spicily with 6% and 9% DPET. However, as shown in Figure 10, there is no apparent change in porosity with 1% and 3% DPET.

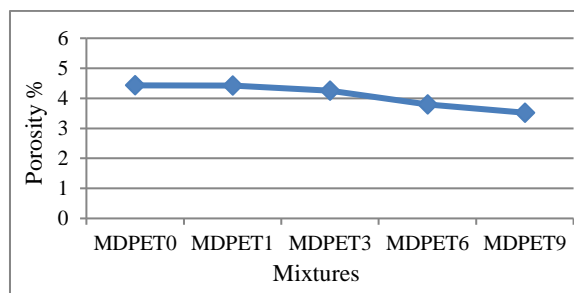


Figure 10. Impact of DPET content on mortar's Porosity.

This drop is due to the fact that DPET contains smaller particles than sand, with an average particle size of 5 microns in DPET. As a result, the DPET particles shut the mortar's capillary tubes. This results in the mortar becoming micro porous [24]. The mortar samples with 1% and 3% DPET, on the other hand, contain a small quantity of DPET and have minimal influence on porosity hence these mixtures have a different porosity approach than the reference mortar.

Conclusions

The current research introduces an alternative utilization of the waste PET water bottles by depolymerized PET and reusing the production in the construction field. The main conclusion remarks are:

1. The bubbles column reactor can save energy and time in waste PET depolymerization.
2. The DPET particles can be used as a modifier in the cement mortar by replacing the sand with the DPET particles.
3. The thermal insulation of the mortar increases when replacing the sand with DPET, and that is because the DPET particles have lower thermal conductivity than that of sand.
4. The mortar density decreases with increases of DPET replacement due to the lower density of DPET particles.

5. The DPET particles have an imperceptible influence on the mortar porosity at lower replacement amounts of 1% and 3%. In comparison, this influence can be indicated when the replacement amount is 6% and 9%. The mortar's porosity decreases in these ratios due to the DPET particles closing the microporous.
6. The reduction in thermal conductivity and density of the mortar containing DPET particles is due to the characteristics of the DPET particles rather than an increase in porosity of the mortar.
7. The plastic DPET particles have a tendency to slow the propagation of heat, which in turn decreases the global thermal conductivity of the cement mortar composite. This may be because of waste PET after depolymerization rather than using it directly in the mortar and uses minimal DPET particles size.

References

- [1]. Tapkire G., Parihar S., Patil P., and Kumavat H. R., Recycling plastic used in concrete paver block", International journal of research in engineering and technology. *International Journal of Research in Engineering and Technology*. **3**(9): p. 33-35(2014)
- [2]. Aiad I., El-Sabbagh A. M., Shafek S. H., Adawy A. I., and Abo-EL-Enein S. A., Effect of Some Prepared Superplasticizers (Cyclohexanone Based) on Compressive Strength and Physico-chemical Properties of Oil Well Cement Pastes. *Egyptian Journal of Chemistry*. **59**(5): p. 851-866(2016)
- [3]. Doyle A. M., Albayati T. M., Abbas A. S., and Alismaeel Z. T., Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin. *Renewable Energy*. **97**: p. 19-23(2016)
- [4]. Abbas R., Shehata N., Mohamed E. A., Salah H., and Abdelzاهر M., Environmental safe disposal of cement kiln dust for the production of geopolymers. *Egyptian Journal of Chemistry*. **64**(12): p. 7529-7537(2021)
- [5]. Rai B., Rushad S. T., Kr B., and Duggal S. K., Study of Waste Plastic Mix Concrete with Plasticizer. *ISRN Civil Engineering*. **2012**: p. 469272(2012)
- [6]. Patil P. S., Behavior of concrete which is partially replaced with waste plastic. *International Journal of Innovative Technology and Exploring Engineering (IJITEE)*. **4**(11)(2015)
- [7]. Asadi I., Shafiqh P., Abu Hassan Z. F. B., and Mahyuddin N. B., Thermal conductivity of concrete – A review. *Journal of Building Engineering*. **20**: p. 81-93(2018)
- [8]. Hussein Z. A., Shakor Z. M., Alzuhairi M., and Al-Sheikh F., Thermal and catalytic cracking of plastic waste: a review. *International Journal of Environmental Analytical Chemistry*: p. 1-18(2021)
- [9]. Real S., Gomes M. G., Moret Rodrigues A., and Bogas J. A., Contribution of structural lightweight aggregate concrete to the reduction of thermal bridging effect in buildings. *Construction and Building Materials*. **121**: p. 460-470(2016)
- [10]. Alshrefy Z. A., Alahmady K. K., Sedeeq L. J., Al-Sharif Z. T., and Moualli N., Physico-chemical survey of bottled and tap water in Iraq. *Journal of Green Engineering*. **11**(1): p. 349-365(2021)
- [11]. yazoghli O., Dheilly R. M., and Quéneudec M., The valorisation of plastic waste: thermal conductivity of concrete formulated with PET, in 1st International conference on engineering for waste treatment. 2005, Springer, Cham: Albi, FRANCE.
- [12]. Wang R. and Meyer C., Performance of cement mortar made with recycled high impact polystyrene. *Cement and Concrete Composites*. **34**(9): p. 975-981(2012)
- [13]. Ferrándiz-Mas V., Bond T., García-Alcocel E., and Cheeseman C. R., Lightweight mortars containing expanded polystyrene and paper sludge ash. *Construction and Building Materials*. **61**: p. 285-292(2014)
- [14]. Záleská M., Pavlíková M., Pokorný J., Jankovský O., Pavlík Z., and Černý R., Structural, mechanical and hygrothermal properties of lightweight concrete based on the application of waste plastics. *Construction and Building Materials*. **180**: p. 1-11(2018)
- [15]. Zizka M., Sulc R., and Dítl P., Heat Transfer Between Gas and Liquid in a Bubble Column. *Chemical Engineering Transactions*. **57**: p. 1261-1266(2017)
- [16]. Shu S., Vidal D., Bertrand F., and Chaouki J., Multiscale multiphase phenomena in bubble column reactors: A review. *Renewable Energy*. **141**: p. 613-631(2019)
- [17]. Rieth I. and Grünewald M., Auslegung von Blasensäulen mithilfe von Compartmentmodellen. *Chemie Ingenieur Technik*. **91**(7): p. 1049-1058(2019)
- [18]. Bombáč A., Rek Z., and Levec J., Void fraction distribution in a bisectonal bubble column reactor. *AIChE Journal*. **65**(4): p. 1186-1197(2019)
- [19]. Alzuhairi M. A. H., Khalil B. I., and Hadi R. S., Nano ZnO Catalyst for Chemical Recycling of Polyethylene terephthalate (PET). *Engineering*

- and Technology Journal*. **35**(8): p. 831-837(2017)
- [20]. Mohammed H., Alzuhairi M., Ibrahim S. I., and Hussein S. S., Ternary waste plastic blends for binding and adhesion. *International Journal of Environmental Studies*: p. 1-11(2021)
- [21]. Salih S. I., Al-gabban A. M., and Abdalsalam A. H., Preparation and Characterization of PMMA-HDPE and HDPE-PMMA Binary Polymer Blends. *Engineering and Technology Journal*. **35**(4): p. 311-317(2017)
- [22]. Mahdi R. S., Al-Zubaidi A. B., and Hashim H. N., Incorporation of Iraqi Rocks in the Production of Eco-Friendly Cement Mortar. *Engineering and Technology Journal*. **38**(10A): p. 1522-1530(2020)
- [23]. Choi Y.-W., Moon D.-J., Chung J.-S., and Cho S.-K., Effects of waste PET bottles aggregate on the properties of concrete. *Cement and Concrete Research*. **35**(4): p. 776-781(2005)
- [24]. Hameed A. M., Alzuhairi M., and Ibrahim S. I., Studying some of mechanical properties and microstructure analysis for cement mortar using waste of depolymerized Polyethylene terephthalate by using bubble column technique. *IOP Conference Series: Earth and Environmental Science*. **779**(1): p. 012097(2021)