

Improving impact energy absorption capacity loss resistivity of thermally cycled cement pastes using a thermoset polymer additive

Eren Kömürlü^{1*}, Atila Gürhan Çelik¹

¹ Giresun Üniversitesi İnşaat Mühendisliği Bölümü, Giresun, Turkey

* e-mail: ekomurlu@giresun.edu.tr, ORCID: 0000-0002-2123-7678

Abstract

A modified silicone type thermoset polymer additive effect on impact energy absorption capacity (EAC) values of cement pastes exposed to thermal cycles in water was investigated with a series of Charpy impact tests. The thermoset type polymer (MSP) material was added with different amounts in the cement and water mixes. The polymeric additive used in this study was in liquid phase while adding into the fresh cement mix and started to solidify by polymerization after being mixed well in the cement paste. The MSP based product was selected to use because of its ability of polymerization in contact with water. Although EAC values of specimens cured under a constant temperature were found to slightly decrease, the strength loss due to thermal cycles was found to be much limited as a result of using the MSP type thermoset additive. Therefore, the additive tested in this study was assessed to improve the impact resistivity of the cement pastes and mortars against the thermal changes. Depending on the additive amount in the mix and thermal change details, MSP added specimens were determined to have notably higher EACs than those of the specimens with no polymer additive.

Keywords: Impact energy, cementitious materials, Charpy test, thermosets, thermal cycling

1. Introduction

Many important seasonal changes like those in temperature, water content and air humidity are generally neglected in civil engineering designs and analyses. In addition to the annual changes, there are also significant daily changes depending on the region climate. The daily changes can be rapid and make damages in repeating periods. In the continental climate, it is possible to see more than 30 °C temperature differences in a day. Especially for long-term service life times of concrete materials, effect of thermal changes in repeated cooling and heating cycles on the mechanical properties is an important topic for engineering projects (Jena and Panda, 2018; Komurlu and Kesimal, 2015). As another matter, water saturated and unsaturated conditions are also important in the seasonal changes effect on the concrete materials. Especially, temperature changes causing the freezing and thawing cycles can make notable damages in case of having water saturated voids.

From the various point of views, their high brittleness can be assessed as the most important disadvantage of concrete materials. The brittle characteristic causes an immediate loss of the load bearing capacity as the maximum load is achieved. The cement paste is the binder matrix in the concrete mixes which are very famous composite materials including aggregates with different size distributions. With an increase in the cement paste material ductility, energy absorption capacities of concrete mixes increase under both static and dynamic load conditions (Fantilli et al., 2016; Sakka and Gilbert, 2018; Pam et al., 2001). The increase of concrete

material ductility supplies significant advantages in different dynamic load conditions like those of earthquake, various impact and repeated loads (Hung et al., 2014; Senthil, 2016; Komurlu and Kesimal, 2012). The high brittleness property also causes the poor thermal resistivity of concrete materials. Because the crack propagation resistivities of the brittle materials are quite poor, they are easily disintegrated owing to the thermal strain cycles.

Polymeric additives are popular to improve crack propagation resistivity, ductility and energy absorption capacity of the concrete materials. In general, polymeric reinforcements are used in the form of fiber additive in the concrete mixes. Use of the fiber reinforcement in the concrete mixes can also improve the resistivity against thermal strains (Yaragal et al., 2015; Yaragal and Ramanjaneyulu, 2016; Marthong, 2019). Besides of the fiber products, a new method of using liquid phase polymers in concrete mixes were investigated within this study.

For the aim of improving cement paste material ductility and the thermal resistivity, a MSP based thermoset was used in the cement and water mix in this study. Because thermoset polymers are in liquid phase before their polymerization reactions, they are usable for homogenization of the cement paste mixes. Effect of the water on thermoset polymerization reactions and self-strength values of the additive are important points in terms of selecting a proper polymer product. Additionally, viscosity and solidification time of thermosets are significant parameters for the workability of the fresh cement mixes. Although polymerization reactions of thermosets are typically completed within a day, a notable solidification only takes one hour. Therefore, fresh cement adhesion to the polymer surfaces is an important factor for the strength of the composite cement pastes.

Within this study, a modified silicone polymer (MSP) product was investigated as a cement paste additive. MSP thermosets are synthetic polymers and also known as modified polysiloxanes or MS Polymers which are used as strong sealants and preferred due to high adhesive performances on both dry and moist surfaces. The MSP is a liquid form of adhesive and looks like a gel before its polymerization. It keeps its elasticity and stability in both high and low temperatures. Furthermore, MSPs which are resistant to moisture and weathering can polymerize and solidify in contact with water (Owen, 2017; Komurlu, 2020; Zander and Peng, 2018; Magalhães et al., 2019). Therefore, it was expected to properly use a MSP based additive in cement paste mixes. The aim of using a thermoset additive is to be a kind of reinforcement in cement mixes. To assess its usability for improving resistivity against different thermal change and water saturation conditions, polymer added cement paste mixes were investigated with a series of dynamic (impact) load tests as detailed in the following title.

In a previous work carried out by Komurlu (2020), the same MSP additive was used and found to improve the ductility of the cement pastes under static loading tests. As a motivation of this study, the impact resistance of cement pastes was predicted to also increase because of the improved ductility property by the additive used.

2. Materials and Methodology

In this study, CEM 1 type ordinary Portland cement was used in the mixes to investigate the effect of the thermoset polymer additive on results obtained from the Charpy impact test. In the mix, the water to cement ratio was 0.45 by weight. There were three different cement mix groups with no polymer, 3% and 6% polymer additives by weight. It should be noted herein

that the percentages are the ratio of polymer additives to total mix (cement + water + polymer) weights. The paste mixes were homogenized in a concrete mixer for 8 minutes. The Charpy impact test specimens were casted into moulds with the the sizes of 22 mm x 22 mm x 80 mm, compacted using thin tamping rods, and put on the vibration table to remove air in fresh mix. The Charpy impact test equipment which is convenient for the cementitious specimens were used in the experimental studies. As the hammer of the Charpy test is dropped, the impact energy was applied on the specimens. The three point bending effect was induced under the immediate load condition as the falling hammer applies load to the specimens. Specimens used in this study is seen in Figure 1. In the Charpy impact test, specimens with the curing time of 14 days were used (Figure 2).



Figure 1. Specimens used in this study



Figure 2. a) The Charpy impact test equipment, b and c) raising the hammer, d) hammer after fall

In this study, the Charpy impact test, a widely applied impact strength determination test for various materials such as metals, polymers, cementitious materials and ceramics was performed to determine the fracture energy of cement paste specimens. In the Charpy impact test, beam specimens are hit by a hammer carried on a pendulum which is allowed to fall freely to supply impact energy. As the hammer hits to a specimen, an amount of energy is consumed for crack propagation. To measure the energy consumption amount, the height difference between the initial position and which the pendulum rises after failure is recorded by a pointer mounted on the dial.

To investigate thermal changes effect on the energy absorption capacity values of the cement paste specimens, a refrigerator at 3 °C and a stove at 90 °C were respectively used for 16 cycles (Figure 3). There were two water tanks in the refrigerator and the stove. Specimens with and without the polymer additive were immersed in the water tanks together and had totally same thermal change procedure in water. After a 5 days curing time, thermal cycles were started. In the thermal change procedure, heating at 90 °C (120 minutes) and cooling at 3 °C (120 minutes) were carried out twice a day for eight days. Specimens were kept out of water at the end of the daily thermal cycles. To speed up the effect of the thermal cycles, temperature changes were applied immediately making a thermal shock in water. At the end of the cycles, specimens were kept out of the water for a day. Specimens which were not exposed to the thermal cycles were cured in the room temperature and not kept in water. Totally, 18 specimens were used in the Charpy test and 9 of them (3 for each MSP amount) were exposed to thermal cycles.



Figure 3. Stove (a) and refrigerator (b) used in the thermal cycles

3. Results

Results obtained from the Charpy impact test are given in Table 1. According to results of this study, impact energy absorption capacity values of cement pastes kept under a constant temperature were found to not highly change with an increase in the amount of the MSP based additive. On the other hand, the MSP additive was found to make specimens more resistive against EAC loss after thermal changes. It is a remarkable outcome of this study to obtain 24% higher EAC values from 6% MSP added specimens in comparison with those of no polymer added and thermally cycled specimens. As seen in Figure 4, the MSP additive supplies improved EAC performances for the specimens after thermal cycles.

Table 1. Results obtained from the Charpy impact test (TC: thermal cycles)

Specimen type	Mean EAC without TC (J)	Mean EAC after TC (J)	EAC loss after TC (J)
Spec. with 0% MSP	61	38	23
Spec. with 3% MSP	57	42	15
Spec. with 6% MSP	55	47	8

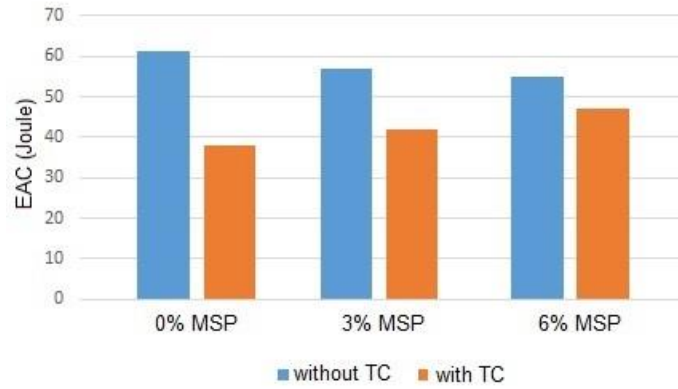


Figure 4. Graphical shown of the Charpy impact test results

4. Discussions and Conclusion

As an advantage of the MSP additive, impact energy absorption capacity (EAC) values of thermally cycled cement paste specimens were found to improve significantly. It is a well-known fact that the EAC values increase with an increase in the ductility (Akhavan et al., 2017; Komurlu, 2019; Najim et al., 2018). Komurlu (2020) reported that the ductility of the cement paste materials are improved by the MSP additive. EAC values and the ductility can be stated to be improved by an increase in the crack propagation resistivity property (Su et al., 2017; Shi et al., 2020; Joshi et al., 2018). Because significant load capacities can be maintained under the plastic strain interval, ductile deformability characteristics of the polymeric materials make their usage advantageous in terms of having high energy absorption capacities (Komurlu and Kesimal, 2017; Komurlu et al., 2017; Wang et al., 2011). Strength is also a determinative property for the EAC values. Instead of a direct EAC improvement, the MSP additive was found advantageous in terms of its supply of EAC loss resistivity against the thermal shocks.

Because mechanical properties of polymer materials vary within a high range, a product should be individually and carefully investigated to assess about its usability (Korey et al., 2020; Komurlu, 2018; Komurlu and Kesimal, 2016). Depending on the production details, same type polymer materials can exhibit significant variations in their strength values. Therefore, self properties of a product should be examined instead of considering typical mechanical property values of a polymer material. Different thermosets can be investigated for the aim of making better strength and ductility properties of cement pastes. The material properties of candidate thermosets should be known before the investigation of usage to foresee an undesired result. For instance, some of the sealants like acrylic based thermoset products have a disadvantage of deterioration because of contacting with water during polymerization reactions (Jiang et al., 2019). It should be reminded herein that the key property of a usable cement paste additive is the ability of proper polymerization in contact with water.

The thermal strains can make significant damages as it is a well-known properties of the brittle concrete materials (Heidari-Rarani et al., 2014; Khan et al., 2020; Baker, 1996). In this study, repeated thermal shocks in water were applied to the cement pastes to investigate whether the thermoset type additive is usable to improve the resistivity against the temperature changes. Depending on the thermal cycle details like temperature differences and the repeat number, the MSP added cement mixes were assessed to be able to have higher impact strength values than those of the specimens without the polymeric additive. Considering the EAC values, thermal resistivity in water was found to be notably bettered using MSP thermoset additive in the mix.

Since the loss in the EAC values are significantly limited by the additive, it is possible to foresee for further thermal cycles to obtain higher differences in the EAC values of MSP added mixes and the specimens without the additive. To deal about costs, it can be noted that price of the additive used in this study is about 4 USD/ kg. In first, the cost may seem a bit high. However, the additive can be economical depending on the engineering aims. The thermal resistivity in water is a quite important property for long-term service life times of various engineering constructions such as piers and concrete footings in water.

As a conclusion, it can be noted that the EAC and thermal resistivity were determined to be improved by using the MSP type thermoset polymer additive. To extend the service life times of concrete materials exposed to the temperature changes in water, the MSP thermoset polymer additive was found to be usable.

Acknowledgement

This study has been supported by FEN-BAP-A 270220-29 coded Giresun University Scientific Research Project

References

- Akhavan, A., Catchmark, J., Rajabipour, F., 2017. Ductility enhancement of autoclaved cellulose fiber reinforced cement boards manufactured using a laboratory method simulating the Hatschek process. *Con Build Mat*, 135, 251-259.
- Baker, G., 1996. The effect of exposure to elevated temperatures on the fracture energy of plain concrete. *Mat. Struct.*, 29, 383.
- Fantilli, A.P., Chiaia, B., Gorino, A., 2016. Minimum reinforcement and ductility index of lightly reinforced concrete beams. *Computers and Concrete*, 18(6), 1175-1194.
- Heidari-Rarani, M., Aliha, M.R.M., Shokrieh M.M., Ayatollahi, M.R., 2014. Mechanical durability of an optimized polymer concrete under various thermal cyclic loadings - An experimental study. *Construction and Building Materials*, 64, 308–315
- Hung, H.H., Liu, K.Y., Chang, K.C., 2015. Rocking behavior of bridge piers with spread footings under cyclic loading and earthquake excitation. *Earthquakes and Structures*, 7(6), 1001-1024.
- Jena, T., Panda K.C., 2018. Mechanical and durability properties of marine concrete using fly ash and silpozz. *Advances in Concrete Construction*, 6(1), 47-68.

- Jiang, B., Oh, K.H., Kim, S.Y., He, X. and Oh, S.K., 2019. Technical Evaluation Method for Physical Property Changes due to Environmental Degradation of Grout-Injection Repair Materials for Water-Leakage Cracks. *Appl Sci*, 9(9), 1740.
- Joshi, S.S., Thammishetti, N., Shanmugam, S.P., Jain, S., 2018. Cracking and ductility analysis of steel fiber reinforced prestressed concrete beams in flexure. *ACI Structural Journal*, 115 (6), 1575-1588.
- Khan, M.S., Almutairi, S., Abbas, H., 2020. Mechanical properties of concrete subjected to cyclic thermal loading. *European Journal of Environmental and Civil Engineering*. DOI: 10.1080/19648189.2020.1782771
- Komurlu, E., 2018. Elastomer type Thin Spray-on Liners Use to Combat Rock Burst, 12th Regional Rock Mechanics Symposium of Turkey (Rockmec2018), Trabzon, pp 255-261
- Komurlu, E., 2019. An Experimental Study on Determination of Crack Propagation Energy of Rock Materials under Dynamic (Impact) and Static Loading Conditions. *Hittite Journal of Science and Engineering*, 6, 1-6.
- Komurlu, E., 2020. An Investigation of Using Thermoset Polymer type Liquid Additives to Improve Cement Grout Performances in Rock Bolting Applications. *International Journal of Geosynthetics and Ground Engineering*, 6, Article no: 52.
- Komurlu, E., Kesimal, A., 2012. New Engineering Materials for Underground Constructions. 16th International Metallurgy and Materials Congress, pp. 307-319, İstanbul, Turkey.
- Komurlu, E., Kesimal, A., 2015. Improved Performance of Rock Bolts using Sprayed Polyurea Coating. *Rock Mech. Rock Eng.*, 48, 2179-2182.
- Komurlu, E., Kesimal, A., 2016. An Experimental Study on Reinforcing Rock Columns using Polymeric Heated Ties. *Rock Mech. Rock Eng.*, 49, 1995-2003.
- Komurlu, E., Kesimal, A., 2017. Experimental Study on Usability of Friction Rock Bolts with Plastic Body. *International Journal of Geomechanics*, 17(9), Paper no: 04017058.
- Komurlu, E., Kesimal, A., Aksoy, C.O., 2017. Use of Polyamide-6 type Engineering Polymer as Grouted Rock Bolt Material. *International Journal of Geosynthetics and Ground Engineering*, 3, Paper no: 37.
- Korey, M., Johnson, A., Webb, W., Dietersberger, M., Youngblood, J., Howarter, J., 2020. Tannic Acid Based Pre-Polymer Systems for Enhanced Intumescence in Epoxy Thermosets. *Green Materials*. DOI: 10.1680/jgrma.19.00061
- Magalhães, S., Alves, L., Medronho, B., Fonseca, A.C., Romano, A., Coelho, J.F.J, Norgren, M., 2019. Brief Overview on Bio-Based Adhesives and Sealants. *Polymers*, 11(10), paper no: 1685.
- Marthong, C., 2019. Effect of waste cement bag fibers on the mechanical strength of concrete. *Advances in Materials Research*, 8(2), 103-115.
- Najim, K.B., Saeb, A., Al-Azzawi, Z., 2018. Structural behaviour and fracture energy of recycled steel fibre self-compacting reinforced concrete beams”, *Journal of Building Engineering*, 17, 174-182.

- Owen, M.J., 2017. Silicone Hydrophobicity and Oleophilicity. *Silicon*, 9, 651–655.
- Senthil, K., Satyanarayanan, K.S., Rupali, S., 2016. Energy absorption of fibrous self compacting reinforced concrete system. *Advances in Concrete Construction*, 4(1), 37-47.
- Pam, H.J., Kwan, A.K.H., Ho, J.C.M., 2001. Post-peak behavior and flexural ductility of doubly reinforced normal and high-strength concrete beams. *Structural Engineering and Mechanics*, 12(5), 459-474.
- Sakka, Z., Gilbert, R.I., 2018. Numerical investigation on the structural behavior of two-way slabs reinforced with low ductility steel. *Structural Engineering and Mechanics*, 65(3), 223-231.
- Shi, X., Brescia-Norambuena, L., Tavares, C., Grasley, Z., 2020. Semicircular bending fracture test to evaluate fracture properties and ductility of cement mortar reinforced by scrap tire recycled steel fiber. *Engineering Fracture Mechanics*, 236, 107228
- Su, Y., Wu, C., Li, J., Li Z.X., Li W., 2017. Development of novel ultra-high performance concrete: From material to structure. *Construction and Building Materials*, 135, 517–528.
- Wang, Y.F., Ma, Y.S., Wu, H.L., 2011. Reinforced high-strength concrete square columns confined by aramid FRP jackets. part I: experimental study. *Steel and Composite Structures*, 11(6), 455-468.
- Yaragal, S.C., Warriar, J. and Podila, R., 2015. Strength loss contributions during stages of heating, retention and cooling regimes for concretes. *Advances in Materials Research*, 4(1), 13-22.
- Yaragal, S.C., Ramanjaneyulu, S., 2016. Exposure to elevated temperatures and cooled under different regimes—a study on polypropylene concrete. *Advances in Materials Research*, 5(1), 21-34.
- Zander, L., Peng, J., 2018. New Silane-Terminated Polymers for Sealants and Adhesives. *Adhesion Adhesives Sealants*, 15, 20–23.