THE OPTIMIZATION OF BIOPOLYMER ADDITIVE CEMENTS ON THE BEHAVIOR OF FREEZING AND THAWING CYCLES

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ABSTRACT
Chitin, which is the most common natural polymer afterward cellulose in the world, are obtained from shrimp, lobster and crab-like arthropods. The actual usegae of chitin is in the branch of biomedical applications. In this study, biopolmer based and chitin added cement was investigated in order to obtain its freeze & thaw resistance values. Chitin was used in replacement of cement by its weight of 0,3 % and 1 %. Due to the viscosity increase caused by natural polymers, three distant chemical additives (polycarboxylates, naphthalene sulphonate or melamine sulphonate) was used at the rates of 0.4 %, 0.8 % and 1 %. 7 and 21 days compressive strenght, flow rate and freze & thaw resistance test were performed on the 21 different mixture at this context. As a result of the optimization following experiments, 0.4 % polycarboxylate based mortar was determined as reflecting best performance. Besides, it has been also found that in sync usage of chitin and chemical additives boosts freeze and thaw resistance. Therefore, biopolymers such as chitin and chitosan can be practiced in the cement and concrete technologies.

Keywords: Chitin, Chitosan, Freeze & Thaw Effect, Durability**,** Viscosity.

1. INTRODUCTION

Chitin is the second most common natural polymer after cellulose. Tis polymer is synthesized by a large number of living organisms. Chitin is a biopolymer which is formed in the cell walls of fungi, eyeats or arthropods' regular crystalline structural exoskeleton (Rinauda 2006). The annual world chitin production is reported to be approximately $15x10^4$ tonnes. This amount is obtained by adding $5,6x10^4$ tonnes (shrimps), $3,9x10^4$ tonnes (various shellfishes), $3,2x10^4$ tonnes (fungis) and $2,3x10^4$ tonnes (oysters). Chitin is found in insect's shells about 23.5 % and it exists in crabs and shrimps in the range of 32 % and 17 % respectively (Guang 2002). Chitin was first used in 1884 and has a great significiance as natural polysaccharide in the present days. Chitin is provided by using various acids for the dissolution of calcium carbonates that are origined from arthropods shells. Afterwards, the product is kept in an alkaline medium for the dissolution of proteins. Besides, in order to attain colorless chitin, decolouration process can be applied (Rinauda 2006). The biggest problem encountered in chitin and chitosan production is high costs. Unit price per kilogram varies 10 to 1000 dolors depending on its production techiques and quality. Nowadays, it changes from 3 dollars to 6 for chitin, 15 dollars to 20 for chitosan (Web Soruce 06.17.14).

Depending on the source, chitin comprises two allomorp as α and β (Rudall KM 1973, Blackwell J 1973). α type chitin is derived from cell walls of fungi, yeats and crab, lobster shells and insect husk (Olivera BM 1995). β type chitin is obtained hardly in the nature due to the reason that it is obtained from the tubes which is synthesized by squid proteins and worms (Blackwell J 1965, Gaill F 1992).

Although there are many variants of the chitin, the most important of these is chitosan (Demir A, 2009). Despite the fact that chitin's and chitosan's molecular stuructures appear similar, their chemical properties are significanlty different. Chitin has higher stability subject to the its intramolecular and hydrophobic structural intereactions or its intramolecular and intermolecular hydrogen bonds. Moreover, having more crystallization leads chitin to be less reactive in discrete applications (Mazeau K 2004).

For biopolymers such as chitin and chitosan, another decisive consideration is their solubility effect. Having multiplexed cationic polarity parts along the cahin of chitosan, increases its electrostatic repulsion and polarity. Solubility degree is one of the critical feature that figüre out chitosan comparing with the chitin. Solubility of chitin is very limited and it is a quite picky polymer considering solvent materials (Tharanathan RN 2003).

Organic polymers such as chitin and chitosan can decrease the pull force of inorganic compounds; therefore, the compressive strenght of materials may be depleted. Comparison of the compounds that have strong bonding with calcium ions as follows: phosphates > carboxylate > amino groups > hydroxyl groups (Wang X, Ma J. 2001).

Biopolymers such as chitin and chitosan can increase viscosity depending on their dosage; however, liquidity of the mix may be reduced. In addition, fluidity and consistency are adversly affected, if high molecular weight having chitosan is gone for the compositions rich in calcium. At low dossages molecular weight of polymer effects the setting time; on the other hand, at high dossages deasitilation of polymer influences the setting time. Chitosan obtained from chitin can be used as retarder in cementitious materials. The usage of chitosan in cementitious materials should be limited in order to reduce solubility in alkaline conditions (Zubiate LM 2012).

Nowadays, acid resistance which is one of the great problems for influencing the durability property of a material has come to the fore in oil industry. For the construction of oil and gas wells, cement based materials are often used (P.C. Hewlett 1998, G. Le Saout 2006). Etching process is applied at certain times in oil wells and this application damages the cement injection mortar locating around the wells. Moreover, etching process causes mortar spills at the cementitious material based surfaces and this happenning results in environmental problems for the long term. Due to the this fact, special tyeps of polymer based materials are commonly used (S. Portier 2009, H.W. Dorner 2002, D.A. Silva 2005). Cement-poylmer based materials have been developed against physico-chemical effects occuring in oil wells and fort his porpuse epoxy is chosen considering its high acid resistance amid polymer materials. However, due to the chemical structure of epoxy resins is harmful to human health. Toxin liquids servicing for the dilution of epoxy resin were used for the test on the animals and negative results (cancer cells defective births, etc) were obtained (E.M. Petrie 2006). For this reason, harmful effects of chemicals on the human health is reduced by using biopolymers such as chitin and chitosan in epoxy cementitious material mixes.

Chitin and chitosan applications are ranked as pharmaceutical, medical, waste water treatment, biotechnology, cosmetics, food, textile and agriculture (Demir A., 2009). In this study, the usage of chitin in cement & concrete Technologies was researched in order to expand its operational properties. In order to develop a cementitious based product against freze & thaw effect that is one of the durability problems, cement/biopolymer mixture was prepared by carrying out experiments on fresh and hardened mortars. According to the results, the optimal model is proposed.

2. MATERIAL AND METHOD

2.1. Material

In this study, CEM I 42,5 R type cement is used as per the standard TS EN 197-1. Chemical and physical properties of cement and chitin are given in table 1.

This research covers the three different types of chemical additives as naphtalene sulfonate, melamine sulfonate and polycarboxylate with divergent active substance. Rilem Cembureau type sand was used as aggregates as per the standard TSE EN 196-1.

Table 1. Chemical and Pyhsical Properties of CEM I 42,5 R type cement

Chemical Composition	(%)	Chemical Composition	(%)
SiO_2	20,31	Al_2O_3	5,64
Fe_2O_3	3,27	CaO	64,02
MgO	1,64	SO_3	2,86
Na_2O	0,87	K_2O	0,80
Loss on Ignition (%)	2,17		
C_3S	C_2S	C_3A	C_4AF
55,55	16,50	9,41	1,48
Fineness (cm^2/gr)	3110		
specific gravity (kg/m^3)	3,10		

2.2. Method

Biopolimeric chitin was used at the replacement ratios of 0,3 % and 1 % by weight of cement. As chitin is increasing the viscosity of the mixture and that leads to negative influences on the flowability, 3 different type super plasticizer were used at the rates of 0,4 %, 0,8 % and 1 %. Flow diameter, 7 and 28 days compressive strenght and 50 and 100 cycles freze-thaw experiments are performed on the prepared mixes. Minitab 17 (Trial Version) software is used in order to calculate the optimum mix ratios from 21 distinct designed mixes.

Freeze-thaw experiments were performed according to standard ASTM C 666. Specimens were subjected to the water curing at the same temperature until 14th day. The samples were removed from the curing pool at the end of 14th day and situated in a freeze-thaw test tank. Specimens were subjected to the freeze - thaw cycles at the temperatures of -17,8°C and +4,4°C. Each cycle comprises 1 hour of thaw and 2 hours of freeze processes, and 50 and 100 cycles were performed for each specimen. For the implementation of freeze-thaw test, a fully automatic device is used as per the ASTM C 666 standard. Before and after freeze-thaw cycle processes, compressive strength tests were performed on samples.

3. RESULTS AND DISCUSSION

Studies on the chitin and chemical additives used in different proportions were prepared and their freeze-thaw effect was investigated. Results are presented below:

3.1. Fresh Mortar Test (Spread Diameter Test)

Effects of chitin ratio, type and dosage of additives on fresh mortar properties are shown in the figure 1. Polycarboxylate based additive showed the best performance in terms of spread diameter when using the chitin at the ratio of 0.3 %. However, spread diameter reduction was observed just after usage of chitin at 0.1 %. Increase of chitin ration in naphthalene and melamine added mixes reduced the spread diameter value. Increase of the chitin ratio has an adverse effect on the viscosity of fresh mortar; so it becomes necessary to use chemical additives.

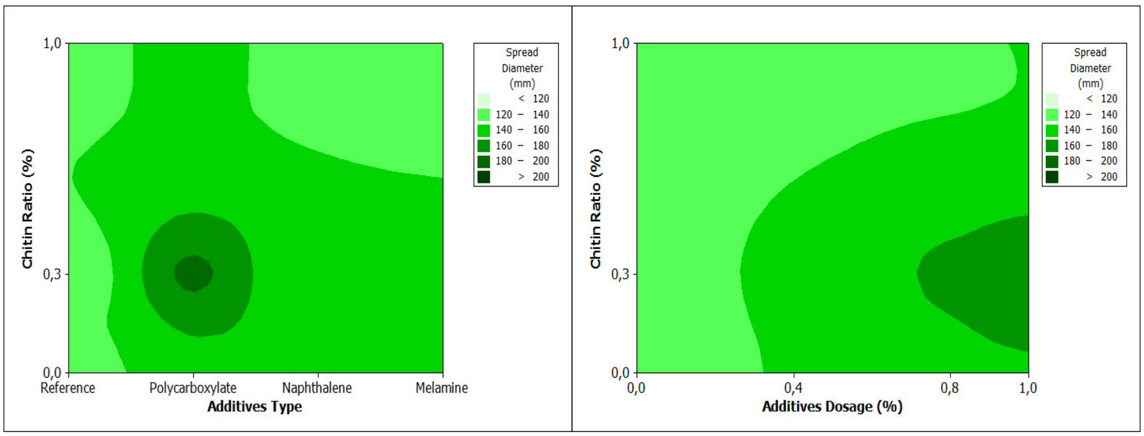

Figure 1. (a) Chitin ratio- additive type (b) the impact of chitin ratio- additive dosage on the features of fresh mortar

When figure 1b was examined, it can be monitored that use of 0.3 % of chitin is highly effective for increasing flow diameter. Particularly, whne using the additive at the dosage rate of 0.8 – 1 %, fresh mortar reflected very satifying performance in terms of fluidity. However, the case 1% of chitin ratio diminishes the efficacy of chemical additives. The increase in use of chitin considerably redounds the need for chemical additives.

The rise of polycarboxylate additive dosage is very effective on the flow diameter as shown in figure 2a. Naphthalene and melamine sulfonate-based additives did not show the same effect. From this study, it can be obtained that the most suitable flow diameter is 150-170 mm for freeze-thaw resistance and above this values, strength and toughness would be negatively effected as in figure 2b.

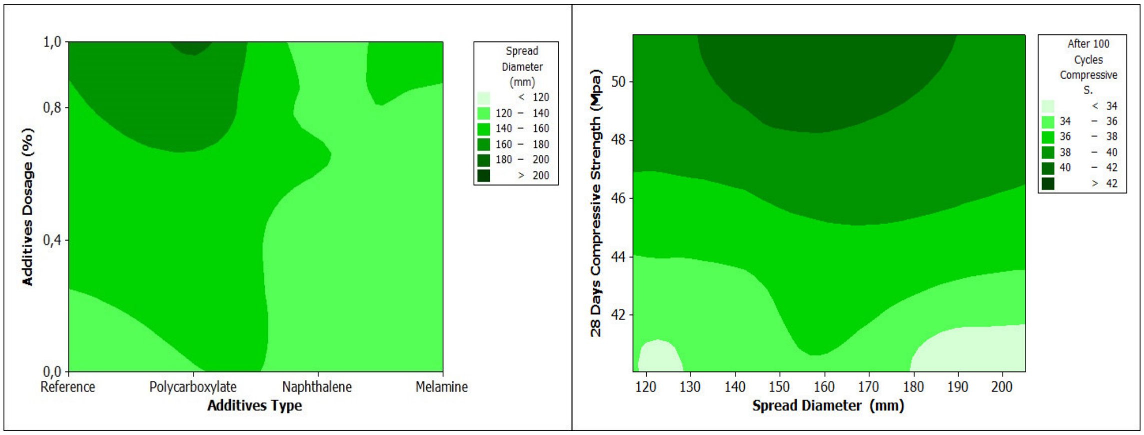

Figure 2. (a) Additive type and the impact of dosage on flow (b) Flow diameter and the impact of compressive strength for 28 days on freeze-thaw

3.2. Hardened Concrete Properties

Chitin ratios and effect of chemical additive types on the compressive strength values after 7 and 28 days are given in figure 3. When figure 3a is examined, the superior compressive strength value for 7 days hardened concrete is obtained in the usage of melamine based chemical additives and 0.3 % of cihitin. However, melamine added mortar compressive strength value dropped if 1 % of chitin is used. The usage of polycarboxylate based additive did not reflect any effect at the rate of low chitin ratios, but increase in chitin ratio was boosted chemical additives effectiveness. This case is explained by the fact that using chitin having lower specific gravity comparing the cement, increases the mortar volume. In order to have a rheologically good performance by using polycarboxylate based additives, fine materials as binder must be used in high volumes. Inadequate performance of polycarboxylate based additives depends on the low usage chitin.

As seen in figure 3b, changes in chitin ratio and chemical additives parameters Show similar features compairing the 7 and 28 days results. High strength values are obtained by using 0.3 % of chitin and naphthalene sulfonate based additives. However, with the increase in the volüme of binding materials, mode of action of these additives is weakened.

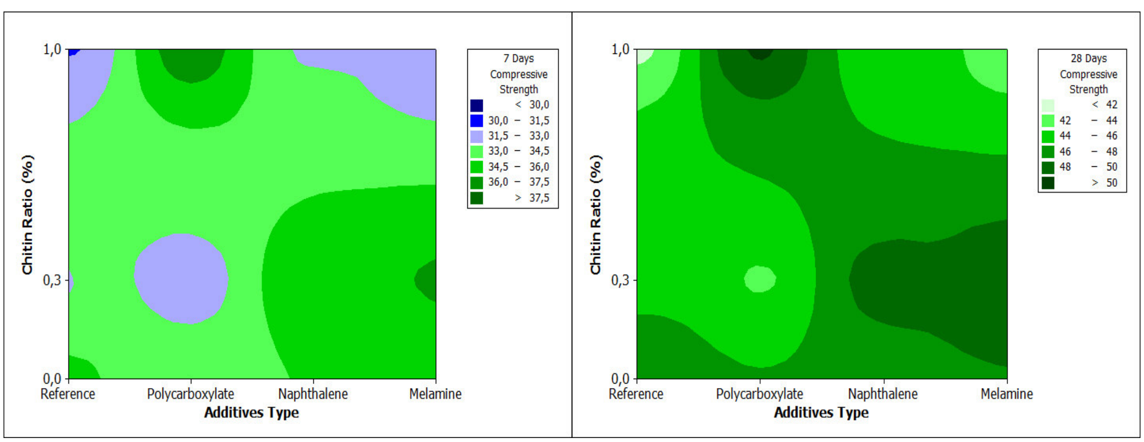

Figure 3. The impact of chitin ratio- additive type on (a) compressive strength for 7 days and (b) compressive strength for 28 days

Although usage of chitin adversely effects the compressive strength, this act on can be decreased by using chemical additives. Increase in chitin ratio negatively effects fresh mortar properties (fluidity); thus, void ratio in mortar rises. In order to avoid this formulation, chemical additives dosages should be increased. Optimum values for 28 days compressive strenghts were obtained at the raios of 0.3 of chitin and 0.4 % of chemical additives as shown in figure 4a.

In figure 4b, the effects of type and dosage of chemical additives on 28 days compressive strength is observed. Polycarboxylate based additives at low rates (0.4 %) have possitive effects on the compressive strength of the specimens. Antithetically, increase in dosage for naphthalene ve melamine sulfonate based additives enhanced compressive strenght values. In case of using 0.4 % of additives, melamine sulfonate based additives led to higher compressive strength values compairing to naphthalene sulfonate based added ones. However, when the chemical additive dosage is 1%, compressive strength values were observed in the opposite situation.

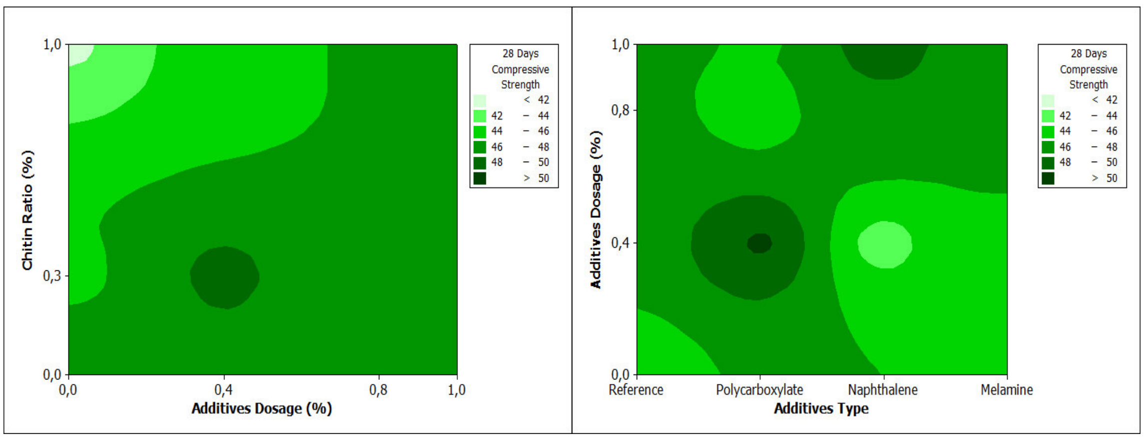

Figure 4. The impact of (a) Additive Dosage-Chitin Ratio and (b) additive type-chitin dosage on compressive strength for 28 days

3.3. Freeze-Thaw Effect

Effects of Chitin and chemical additives types on the 50 and 100 freeze-thaw cycles are given in the figure 5. In case of using 0.3 % of chitin, melamine and naphthalene sulfonate based additives provided higher strenght values against freeze and thaw effect. Subsequent to 50 and 100 cycled freeze-thaw tests, mortar produced with melamine sulfonate additives reflected more superior strength values comparing to naphthalene ones. Nonetheless, with the increase of chitin proportion in melamine sulfonate-based additives added mortar, less strenght values were obtained.

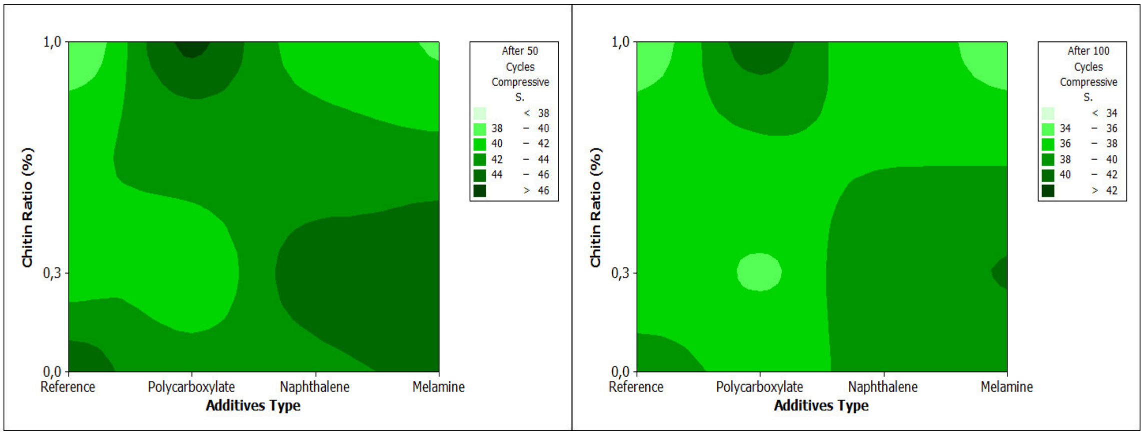

Figure 5. The impact of additive type-chitin ratio on (a) 50 freeze-thaw and (b) 100 freeze-thaw cycles

Polycarboxylate based mortars produced with the contribution rate of 0.3 % of chitin were adversly effected against freeze and thaw cycles. In case of using 1 % of chitin, durability characteristics of mortars improved due to betterment of impermeability features. Beside increase in chitin amount, binder ratio in mortar soared; thus the mechanism of action of chemical additives also increased. Due to the increase in the volume of fine material, void ratio was reduced and more durable and freeze-thaw resistant materials were obtained.

Freezing of the water in the concrete is a slow process. One of the most important factors affecting the freezing speed is void diameter. Formed energy during icing process on the void surfaces and decrease in void water potential energy led to low freezing point of water in mortar. Depending on the various void diameter in mortar, less than a half of water freezed at -30 ^{o}C and remaining is at -60 ^{o}C. Even after pore water turns to ice, a thin film of water remains on the surface. Figure 6 show the relations amid freezing point of pore water and pore diameter. However, if the concrete is fully saturated with water, evaporation does not occur naturally. Due to the frozen water's volume increase in hardened concrete (9 % app.), the hydraulic pressure occurs in thme concrete form (Baradan vd. 2010).

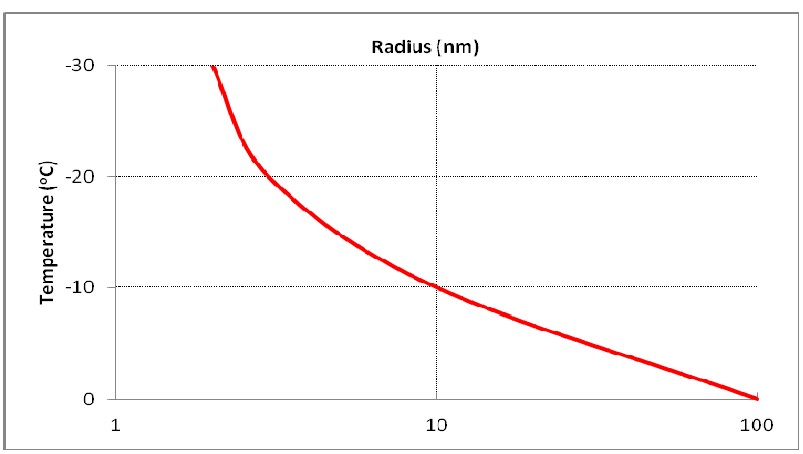

Figure 6. The impact of capillary break diameter on freezing temperature

Usage of polycarboxylate based additives in low dossages yielded positive results, after 100 cycled freeze-thaw processes (Figure 7). However, increasing the dossages of chemical additives negatively effected the freeze-thaw resistance.

Naphthalene sulfonate based additive at 0.4 % showed poorer performance for compressive strenght to match with the reference specimens. Notwithstanding, high strenght values were obtained following 100 freeze-thaw cycle from % 1 naphthalene sulfonate added mixes.

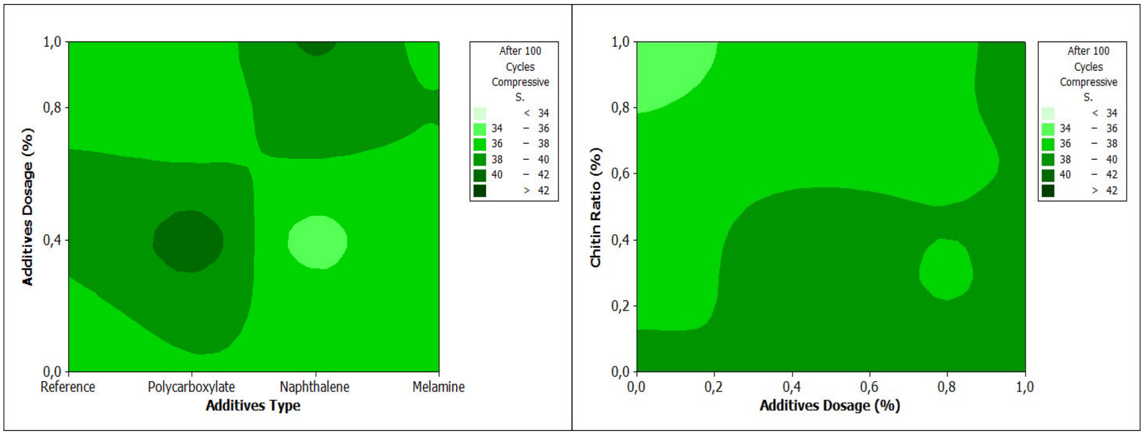

Figure 7. The impact of (a) Additive dosage- additive type and (b) chitin ration- additive dosage on compressive strength after 100 freeze-thaw cycles

Following 100 freeze-thaw cycles, it can be seen in figure 7b that increase in chemical additives dossage leads to an increase in compressive strenght. In case of increasing chitin ratio and curbing chemical additives amount, mortar's freeze-thaw resistance was adversely effected. Freeze-thaw resistance was boosted by adding chemical additives to the mortar. In this case, mortar freeze-thaw events illustrate the importance of the macro pore structure within the mortar.

Spread diameter was incerased by adding polycarboxylate based additives; however, compressive strength and freeze-thaw resistance properties of the specimens were resulted in low values. This event is clarified in two ways : (1) Increased chemical additive dosage developed rheological properties of the mortar and more homogeneous structure were obtained. Due to the obtained nonporous structure mix water can not penetrate in to mortar and hydration processes are negatively developed during the curing mechanism. (2) Unhdrated cement particles following the 28 days curing duration lead to decrease in compressive strength values depending on the freeze-thaw event.

3.4. Optimization

Suitable mixture was identified using optimization method with MINITAB 17 (Trial Version) software upon acquisition of the empirical data. Table 2 shows the purpose functions, references and the comparison of the optimum mixture used in the optimization process. The most suitable material was found to be the mixture produced using no chitin and an additive based on 0.4% polycarboxylate as a result of the optimization. The reason behind not using chitin in the optimum mixture is that chitin reduces the structure of breaks and capillary break diameter given the increased binding volume as a result of chitin use. Water frozen in the capillary breaks damages the structure of mortar at a greater degree due to hydrostatic pressure as a result of the reduced capillary break diameter. It was found that biopolymers increase the freeze-thaw strength using chemical additive. Especially in the case of chitin use, with the reduced break diameter, the use of an air-entrainer will minimize the damage caused by freeze-thaw by generating the necessary break size for frozen water.

Table 2. Comparison of Optimum and Reference Mixtures

<table>
<tr><th>Objective Function</th><th>Condition</th><th>Reference Mix</th><th>Optimum Mix</th><th>Variation (%)</th></tr>
<tr><td>Spread Diameter (mm)</td><td>Maximum</td><td>134</td><td>175</td><td>↑ 30,6</td></tr>
<tr><td>7 Days Compressive Strength (MPa)</td><td>Maximum</td><td>34,72</td><td>37,08</td><td>↑ 6,8</td></tr>
<tr><td>28 Days Compressive Strength (MPa)</td><td>Maximum</td><td>47,56</td><td>50,90</td><td>↑ 7,0</td></tr>
<tr><td>After 50 F-T Compressive Strength (MPa)</td><td>Maximum</td><td>44,87</td><td>48,40</td><td>↑ 7,9</td></tr>
<tr><td>After 100 F-T Compressive Strength (MPa)</td><td>Maximum</td><td>39,04</td><td>41,92</td><td>↑ 7,4</td></tr>
<tr><td>After 50 F-T / Strength Loss (%)</td><td>Minimum</td><td>5,66</td><td>4,66</td><td>↓ 17,7</td></tr>
<tr><td>After 100 F-T / Strength Loss (%)</td><td>Minimum</td><td>17,91</td><td>17,65</td><td>↓ 3,6</td></tr>
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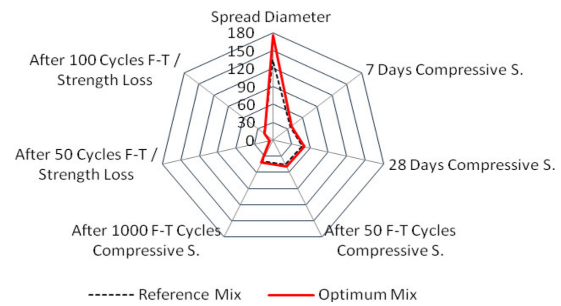
<tr><td rowspan="3">
</td><td>Additive Dosage (%)</td><td>0</td><td colspan="2">0,4</td></tr>
<tr><td>Additive Type</td><td>-</td><td colspan="2">Polycarboxylate</td></tr>
<tr><td>Chtin Ratio (%)</td><td>0</td><td colspan="2">0</td></tr>
</table>

4. CONCLUSION

Freeze - thaw effects, freash and hardened mortar properties were investigated by using vaious chitin and chemical additives over 21 different mixes. In conclusion, the experimental results obtained are summarized as follows:

- Using chitin and polycarboxylate additives in biopolymeric cement based mortars provided more positive results. In case of using melamine and naphthalene sulfonate-based additives, their dosages should be increased.
- Considering the 7 and 28 days compressive strength values, increase in chitin amount in polycarboxylate added mortars yielded more positive results comparing the other produced mortars. Using polycarboxylate additives also exposed the priority of the volume of the fine materials.
- Compressive strength values increased, conceding that the dosage of the naphthalene and melamine sulfonate based additives were rised. However, the increase of polycarboxylate-based additive dosage led to a reduction in compressive strength values. The reduction of pore volume within the structure of mortar reflected that curing processes are adversely affected.
- In case of using chitin at 0.3 %, naphtalene and melamine sulphate based mortar provided more resistance values against freeze and thaw effect. On the otherhand, usage of 1 % of chitin with polycarboxilate based chemicals, resulted in superior performance counter to freeze and thaw effect.
- By using more chemical additives in produced mortars, less capillary voids were obtained; therefore structural elements poured with this mix type indicated more resistance to freeze and thaw effect.
- Using natural polymers in calcium-rich mixes decreases viscosity property of the mortars. To reduce this effect, it becomes necessary to use the superplasticizers.
- It has been proven the availability of usage of chitin in cement industry if high costs are decreased. More resistant and durable structures will be obtained within the use of the chitin in the production of cement.

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