The International Journal of Energy & Engineering Sciences, 2024, 9 (1) 29-41
ISSN: 2602-294X - Gaziantep University

SUPER PLASTICIZER POLYMER SYNTHESIS AND APPLICATION AREA

Onur Davuça, Canan Uraz*

Chemical Engineering Department, Faculty of Engineering, Ege University, İzmir, Turkey.
*Corresponding author e-mail: canan.uraz@ege.edu.tr

ABSTRACT
In this study, it is aimed to synthesize more environmentally friendly and low-cost biopolymer based super plasticizers (SP) by using biopolymers (starch, chitosan polysaccharide, floral oils, etc.), acrylic acid, maleic anhydride, sodium vinyl sulphonate and various corn starches and various catalysts. These raw materials have been examined in terms of their water holding capacity, viscosity, bond structures and renewability. For the structure determination of the synthesized products, FT-IR, fluidity and compressive strength tests are performed. Because it is aimed also to meet the local consumption of cement materials additives in Turkey. In this process, it is to protect our environment by making it bio-based as much as we can, away from today's chemicals and petroleum derivatives. Three different types of polymer are synthesized: flower oil, bowine gelatine and mpeg5000. The ratio of sand: cement: water in the cement mixture used in the study is 2:1:0.45. Synthesized SP polymers were added to the cement mixture at a rate of 0.75%. In the experiments by connecting a plurality of parameters when selecting the appropriate optimal values according to the appropriate product and polymerizing bond products it was synthesized. FTIR results match the peaks in each raw material. So detailed generalization of the bond structure is appropriate. It can be said that bio raw material synthesis is encouraging in the future, and it can be found that form the compressive strength test, the flower oil being more resistant. As a result of this study, three types of polymeric additives were successfully synthesized, analyzed, and performance tests were completed.

Keywords: Superplasticizer, Polymer, Cement.

1. INTRODUCTION
In recent years, with the rapid advancement of high-performance concrete technology, some high-performance components such as chemical additives that can aid concrete have to be developed.
Today, concrete is a material, which is obtained by drying a mixture of cement, sand (aggregate) and water. By changing the ratio of water, sand and cement, it is possible to obtain concretes with different physical properties and application areas. For a cement mixture prepared to be used in ready-mixed concrete;

- Fluid
- Low water content
- It must be in a form that dries quickly and does not solidify [1].

As the water ratio in the mixture increases, the concrete becomes softer and more fragile, whereas reducing the water ratio enhances the concrete's resistance to pressure. However, cement mixtures with low water ratio are not fluid and difficult to form into molds [2, 3].

Despite its low water content, various additives have been developed to achieve cement mixtures that are fluid and retain their fluidity. These materials are known as plasticizers and super plasticizers. As shown in the Table 1, plasticizers and super plasticizers are chemical structures that can reduce the water requirement of the mixture by 15% to 30%, respectively, without disturbing the fluidity of the cement mixture. While plasticizers are generally used in PVC additives, SPs are generally used in cement-based materials to reduce the need for water. Examples of SPs are sodium salts of lignosulfonates, polycarboxylate esters, phosphate or sulphate-terminated polyether's and derivatives [3, 4].

Table 1. Plasticizer and Super plasticizer comparison [1]

Plasticizer	Super Plasticizer
It provides fluidity to a material	It provides fluidity to a material
It reduces the water requirement in the cement mixture by 5-15%	It reduces the water requirement in the cement mixture by 30%. It can give additional properties (strength, flexibility, etc.) to concrete
It is added to the cement mixture between 0.5-3%	It is added to the cement mixture between 0.1-1.0%

Due to the increasing use of super plasticizer as raw materials, its importance is increasing day by day and it is used in many new fields such as construction, agriculture and plastics. To reduce imports of this product and meet demand, this study aims to synthesize Super Plasticizer (SP) compounds with an innovative approach.

1.1 Super Plasticizer Working Mechanism

The main features that SP polymers added to the cement mixture should have;

- It must be dissolved in water.
- It should have a straight chain with negatively charged terminals.
- It should have polyether or polyester groups attached to a negative-ended straight chain.
- It should be well adsorbed on cement particles [5-7].

Some polymers adhere to the surface of metal oxides (CaO, Al_2O_3, SiO_2-based minerals), which are the main ingredients of cement. Thanks to this interaction, a polymeric structure enters between the non-fluid metal oxide surfaces in the cement mixture. If there are no side groups grafted onto the SP polymer, the interaction between cement particles can only be partially prevented [5, 8]. When polyether, polyester, or alkyl groups are "grafted" onto straight-chain negatively charged polymers, the polymer can readily detach the particle it is attached to from other cement particles, owing to its side chains. In this way, cement-cement interaction is greatly reduced, and the mixture becomes fluid [4, 5].

1.2 Importance of the Study

Today, the usage areas of polymers are gradually expanding and as a natural result of this, their importance is increasing. Significant progress has been made in revealing and developing different properties of polymers, which have many areas of use, especially industrially [8, 9]. Super plasticizer raw materials that form in Turkey and are being supplied from abroad. In addition, as restrictions have been imposed on the international import part of Super Plasticizers, the importance of Super Plasticizers has increased in cement and similar sectors in Turkey. Therefore, the study aims to synthesize various raw materials for Super Plasticizers sourced from the domestic market. Fluidization, water absorbency, and water retention are crucial factors in the applications of Super Plasticizers. Many researchers investigated the effects of Super Plasticizers on water absorption capacity and fluidity by changing the reaction parameters [10, 11]. For concrete and other cement mixtures, super plasticizers encourage early mechanical strength development, less foaming and longer workability of fresh concrete. Superplasticizers can be obtained by reacting non-acidic, non-neutralized, polycarboxylic polymers with monofunctional polyether's and nonfunctional polyether's in the absence of strongly acidic catalysts [12, 13].

Superplasticizers generally work with the mechanism described in Figure 1. The biggest factors affecting their performance are;

- Charge/Ma ratio of polymer,
- It is the chain length of the grafted ether, ester or alkyl groups.

In order for SPs to have high fluidizing power, the Charge/Ma ratio should be large, and the side chains should be long. However, since the charge/Ma ratio will decrease as the side chain length increases, the synthesis parameters should be well studied and the ideal chemical structure should be found [7, 14].

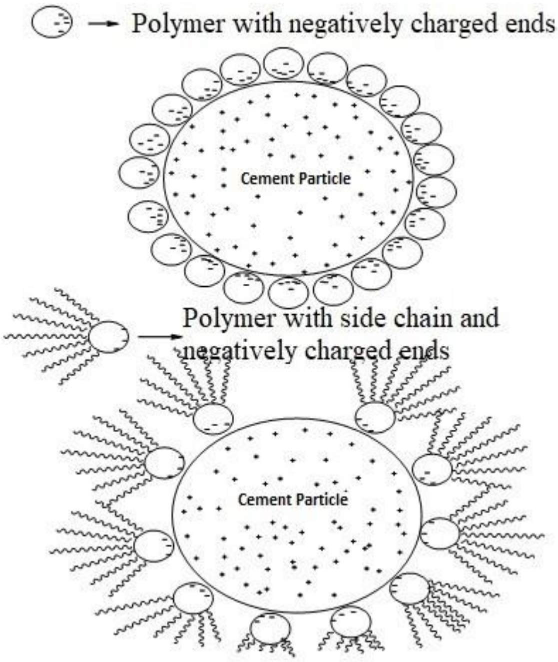

Fig. 1. Superplasticizers working mechanism

2. MATERIALS AND METHOD

2.1 Materials

Huntpol AA is a polymerized acrylic acid product of Viking Company Inc. This product will be used as the main chemical raw material in these syntheses. It was used as straight chain polymer with negative ends.

The following raw materials were used to create side chains that attach to the negatively charged ends: Mpeg 5000 chemical, sunflower oil, beef gelatin product.

Mpeg 5000 chemical is a chemical product used to compare the physical and structural tests of biological products with a molecular weight of 5000 daltons, supplied from the supplier of Sigma Aldrich. Sunflower oil used in the experiments is sunflower oil purchased from the markets. This is the reason why it is used in large quantities and economically in Turkey. Beef gelatin product was obtained from Sigma Aldrich company and is a bio product with a protein basic structure.

- Huntpol AA } Used as straight chain polymer with negative ends.

- MPEG5000 Sigma Aldrich
- Flower Oil
- Beef Gelatin

} Used to form side chains that attach to the negatively charged ends.

2.2 Method

The ratio of sand to cement to water (sand:cement:water) in the cement mixture used in the study is 2:1:0.45. Synthesized SP polymers were added to the cement mixture at a rate of 0.75% (Basis is 100 kg). Addition of 0.75% to the cement mixture can be done in two ways;

Based on the proportions in the mixture, sand and cement are mixed. Then, polymer and water are added to a separate container and the polymer is dissolved in water. The pH value of the solution is brought between 7-8 with sodium hydroxide and added to the cement mixture.

The SP polymer is dissolved in water and the pH is adjusted to 7-8 with sodium hydroxide. Subsequently, the water in the environment is removed. Thus, the obtained polymer changes from the acidic form to the sodium salt form. The product, which becomes powder when dry, is added to the cement-water-sand mixture at a rate of 0.75%. All experiments in the study were carried out in an open system, in a silicon bath, with a magnetic stirrer. Reactions were terminated when water escaped from the medium.

2.3 Superplasticizer Polymer Synthesis

2.3.1 Epoxy Sunflower Oil – Huntpol AA Synthesis (Pol-1)

Industrially available sunflower oil was added to the reaction vessel. Then, formic acid and hydrogen peroxide were mixed in a beaker and added dropwise to the reaction medium. At this stage, the temperature of the reaction medium was kept constant at

The International Journal of Energy & Engineering Sciences, 2024, 9 (1) 29-41
ISSN: 2602-294X - Gaziantep University

60˚C. Since the epoxying reaction is exothermic, this step of the synthesis was performed in an ice bath. The epoxied sunflower oil was washed with water and the excess formic acid and hydrogen peroxide remaining in the medium was extracted. Then, the obtained epoxy sunflower oil was mixed with acidic Huntpol AA at a ratio of 1:1 by weight. The ambient temperature was maintained between 90˚C and 100˚C. The experiment was terminated when all the water had been removed. Epoxying and binding of flower oil to polymer is given in Figure 2.

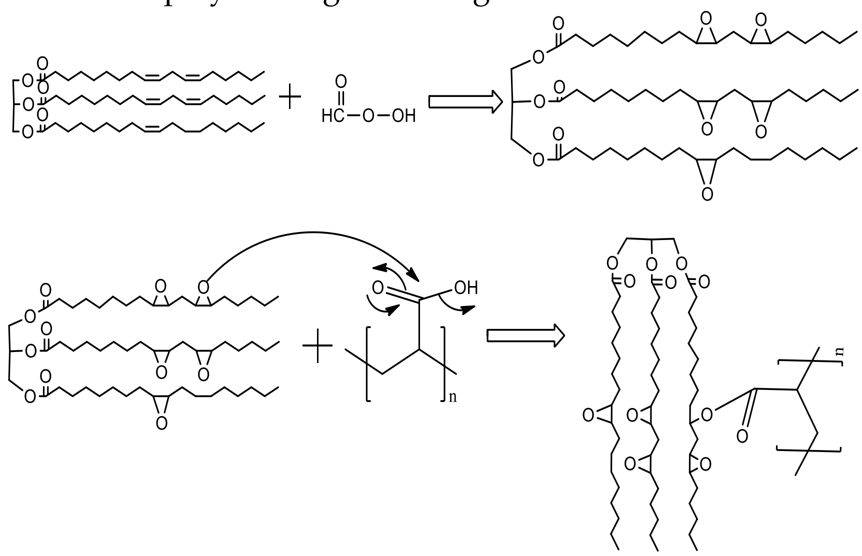

Fig. 2. Epoxy Sunflower Oil – Huntpol AA Synthesis

2.3.2 Beef Gelatin – Huntpol AA Synthesis (Pol-2)

10g bovine gelatin was dissolved in 50 mL deionized water at 60 ˚C. Then, 10 grams of acidic Huntpol AA was added to the medium. The reaction medium was fixed at 90˚C. The reaction was finished when the water output in the medium was finished. The reaction between beef gelatin and Huntpol AA is shown in Figure 3.

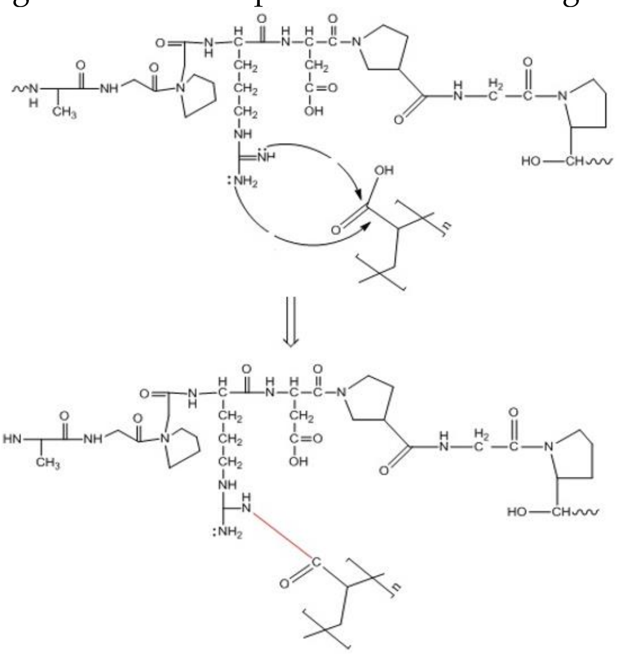

Fig. 3. The reaction between Beef Gelatin and Huntpol AA (Pol-2)

2.3.3 MPEG5000 – Huntpol AA Synthesis (Pol-3)

100g of MPEG (Poly(ethylene) glycol monomethyl ethers)) 5000 was weighed into the reaction vessel and melted at 80°C. Added 100g Huntpol AA on top of MPEG5000. The reaction started when the ambient temperature was 130˚C. Since it is an endothermic reaction, the reaction accelerated as the temperature increased, but the ambient temperature was kept between 130˚C and 140˚C to prevent thermal degradation. Reaction terminated when water output is finished (Figure 4).

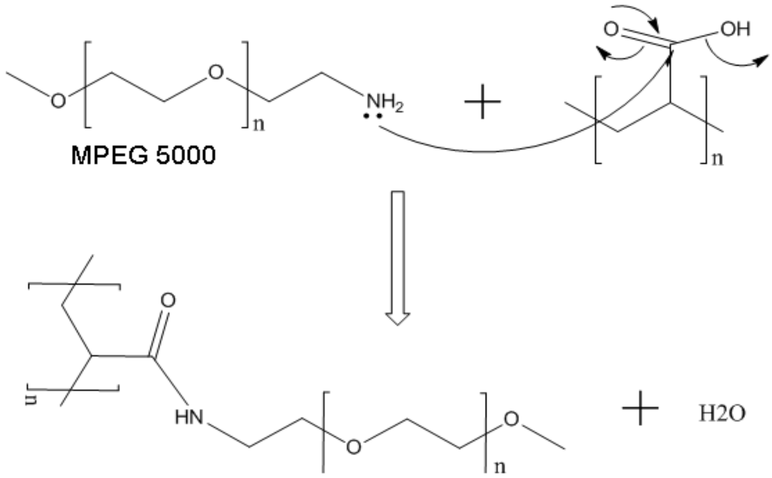

Fig. 4. MPEG5000 – Huntpol AA Synthesis (Pol-3)

3. RESULTS AND DISCUSSION

3.1 Epoxy Sunflower Oil –Huntpol AA (Pol-1)

Fourier-Transform Infrared Spectroscopy (FT-IR) is used for the structure determination of the synthesized products. In the 1000 - 550 cm^{-1} region, vibration bands corresponding to Si and Al are detected in cement. Calcium silicates are present in this region (960 and 970 cm^{-1}). C-vibration bands in the region of 1500 - 700 cm^{-1} (CO). However, secondary bands are also present in the 2923 cm^{-1} region associated with the mineral calcite. Vibration and deformation bands of the constitutive water (OH) are observed in the 3450 - 3400 cm^{-1} and 1650 - 1620 cm^{-1} regions as well [15].
Pol-1 contains the peaks of characteristic ester bonds found at 1741 cm^{-1} (C=O) 1561 cm^{-1} (C=O) and 1279 (C-O) cm^{-1} of epoxidized floral oil (Figure 5).

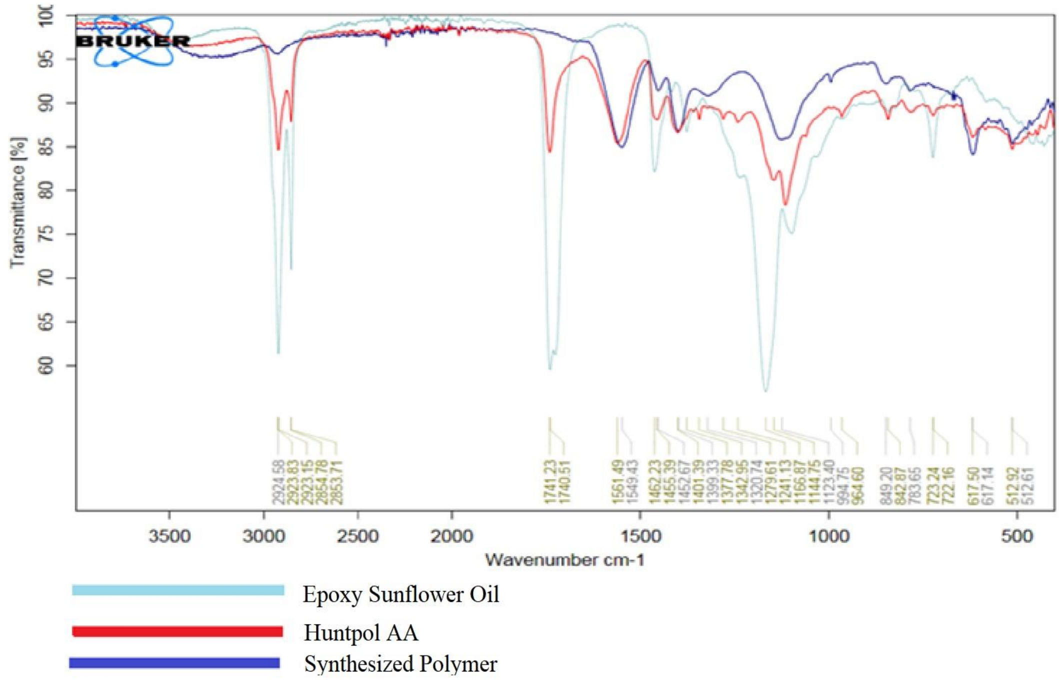

Fig. 5. Bond structures Epoxy Sunflower Oil –Huntpol AA

3.2. Beef Gelatin–Huntpol AA (Pol-2)

The bonds at Pol-2, 1627 cm^{-1} and 1230 cm^{-1} are the characteristic peaks of N-C bonds found at the junction of bovine gelatin and polymer (Figure 6).

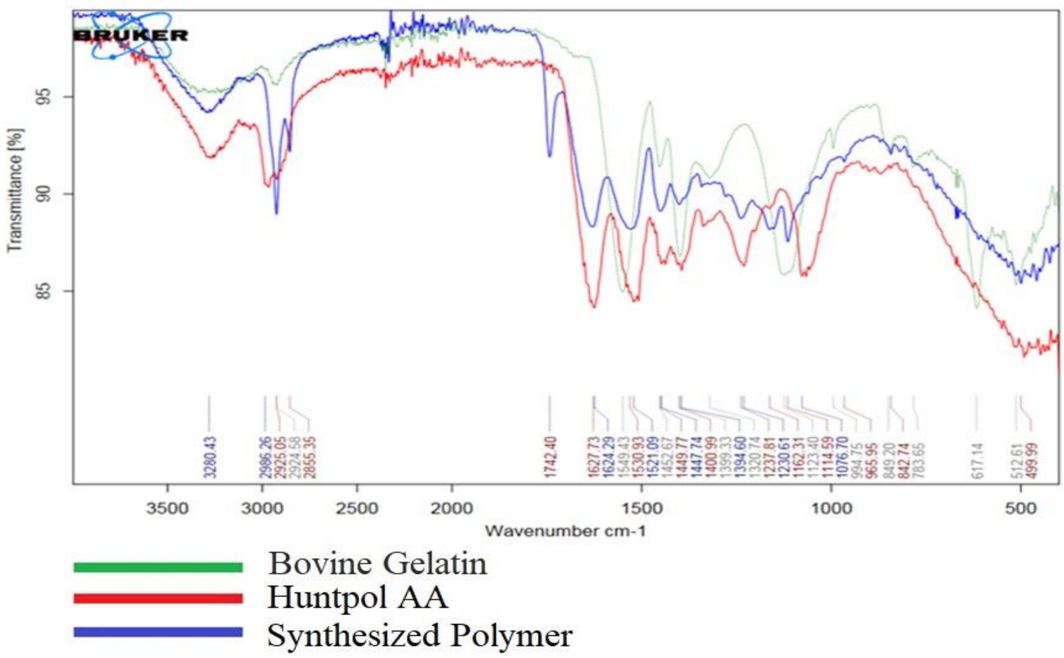

Fig. 6. Bond structures Bovine Gelatin–Huntpol AA (Pol-2)

3.3. Mpeg 5000 – Huntpol AA (Pol-3)

Poly-3 contains all the characteristic peaks belonging to the MPEG-5000 and Huntpol AA the material (Figure 7).

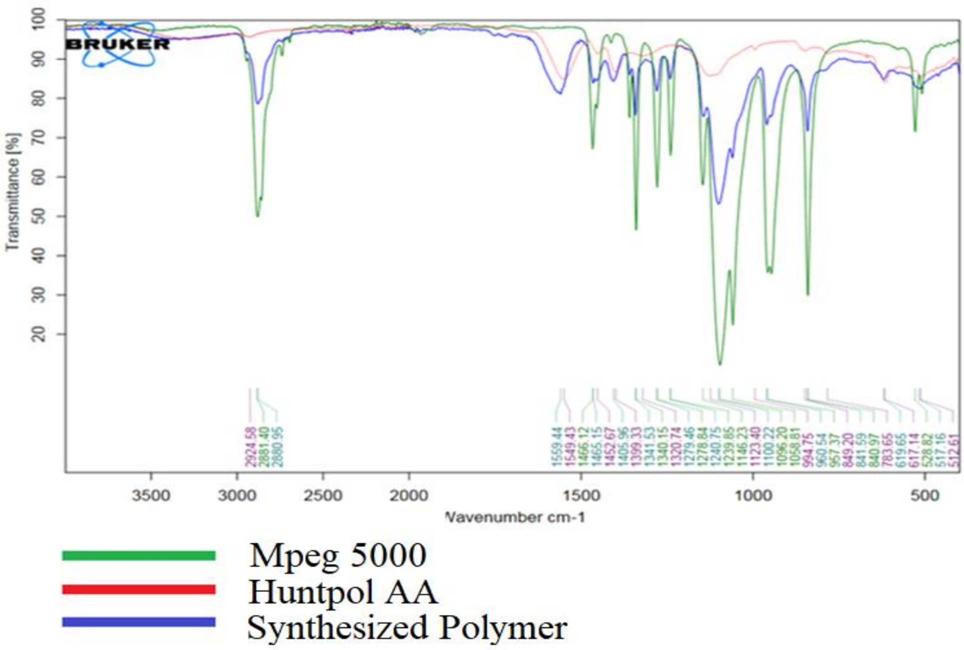

Fig. 7. Bond structures Mpeg 5000 – Huntpol AA (Pol-3)

When the FT-IR diagrams are examined, it is seen that all three polymers (pol-1, pol-2, pol-3) contain characteristic groups of the materials that compose them.
In Pol-1 and Pol-3, there is no peak of the bond formed at the bonding point of the materials, because these bonds (internal amine N-C and ester O-C=O) are already present in the reagents used in Pol-1 and Pol-2 synthesis.

3.4. Fluidity Test

A truncated cone-shaped plastic with a base diameter of 10 cm and an upper diameter of 7 cm and a height of 10 cm was placed on a slightly moistened metallic flat plate (Figures 8 and 9). Cement mixes (1.2 kg) were poured into the truncated cone. The cone was then quickly lifted, and the cement mixture was allowed to spread over the surface for 60 seconds. The diameter of the circle formed by spreading the cement mixture was recorded [16, 17].

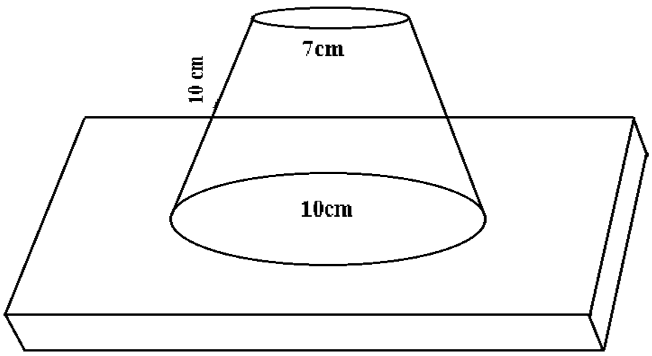

Fig. 8. Fluidity test of cement paste

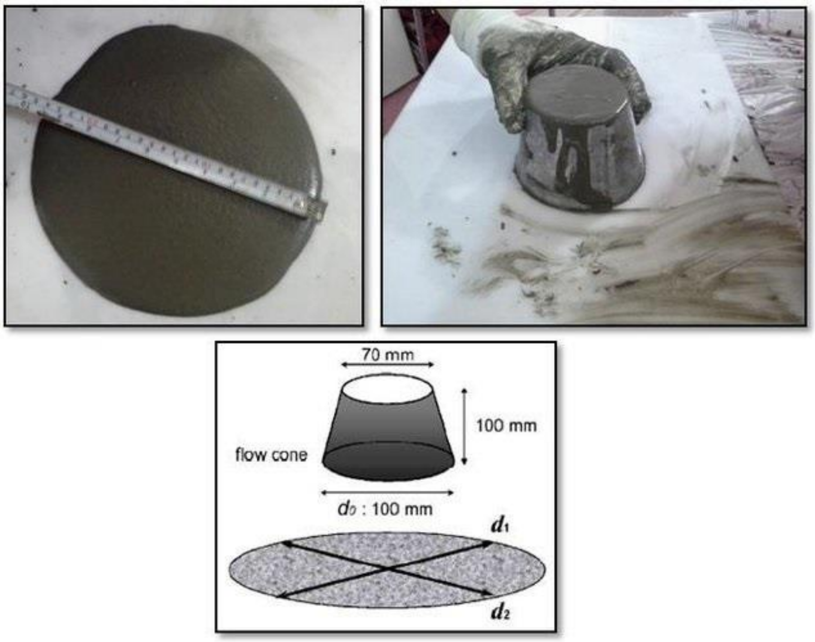

Fig. 9. Fluidity diffusion test [17]

Werani and co-workers also suggest that MPEG-PCEs with shorter graft chains exhibit higher tolerance to montmorillonite as compared to the ones with longer side chains [18]. For this reason, it is seen that additives with long chains spread less than other substances with short chains. The fluidity of cement mixtures with additives is close to each other. Synthetic Pol-3 (MPEG5000-Huntpol AA) showed 450 mm, semi-synthetic Pol-1 (epoxy sunflower oil-Huntpol AA) 410 mm and Pol-2 (Bovine Gelatin-Huntpol AA) 390 mm. A cement mixture containing the same ratio of water (Water:Cement 0.45) with additive polymers has a flow of 200 mm, and a cement mixture containing a sand:cement:water ratio of 2:1:0.8 without any additives has a flow of 400 mm in shown Figure 10. The water ratio (Water:Cement) had to be increased to 0.8 in order for the cement mixture without SP additives to have the same fluidity as the mixtures with additives.

- Pol-1 Sunflower oil - Huntpol AA added (Water:Cement ratio 0.45)
- Pol-2 Bovine Gelatin - Huntpol AA added (Water:Cement ratio 0.45)
- Pol-3 MPEG5000 – Huntpol AA added (Water:Cement ratio 0.45)
- Pol-0.45 Admixture-free cement mixture (Water:Cement ratio 0.45)
- Pol-0.8 Admixture-free cement mixture (Water:Cement ratio 0.8)

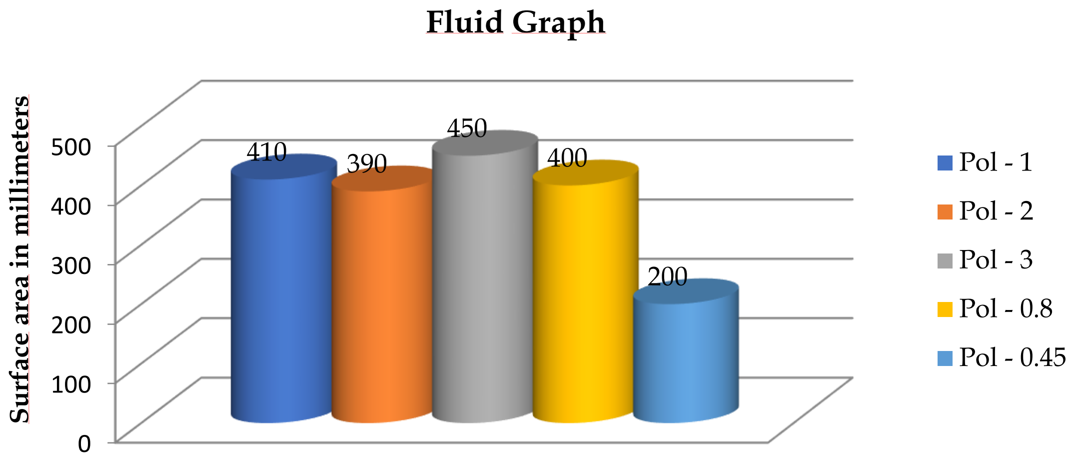

Fig. 10 Description of the data shown in the Fluid Graph

3.3 Compressive Strength Test of Concretes

In order to determine the effect of additives added to cement on concrete strength, four concrete molds were prepared. The ratio of Sand:Cement:Water in SP added mixtures poured into molds was adjusted as 2:1:0.45. Compressive strength was determined by cube sample after 28 days according to ASTM Standard C39/C39M (ASTM Standard).

- Add 0.75% pol-1 (Epoxy sunflower oil-Huntpol AA) to the mixture,
- 0.75% pol-2 (Bovine Gelatin-Huntpol AA) to the second mixture
- 0.75% pol-3 (MPEG5000-Huntpol AA) was added to the mixture.
- The mixture does not contain polymer additives (Pol-0.8). Sand: Cement: Water ratio is 2:1:0.8 as shown in Figure 11.

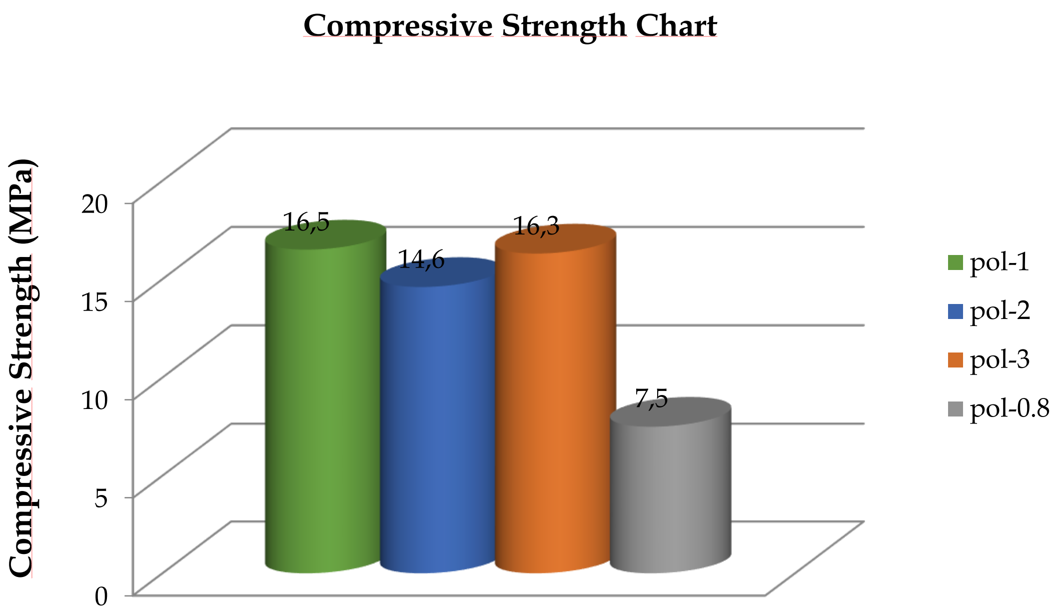

Fig. 11. Compressive Strength Chart and Compressive Strength (MPa)

The International Journal of Energy & Engineering Sciences, 2024, 9 (1) 29-41
ISSN: 2602-294X - Gaziantep University

The results of the compressive strength tests carried out within the scope of the project are as follows;
Compressive Strength Test of Concrete Equipment's;

- Compression Testing Machine
- 15 cm Cube Mould

The resulting mixtures were dried at 20˚C for 28 days in accordance with the standard method. The obtained dry concrete molds were subjected to cubic compressive strength tests. Additive-free concrete, which has the same fluidity as admixture mixes and has a sand:cement:water ratio of 2:1:0.8, shattered while being removed from the mold. The compressive strength of the crushed concrete has been calculated approximately with the help of the graphic (Figure 12).

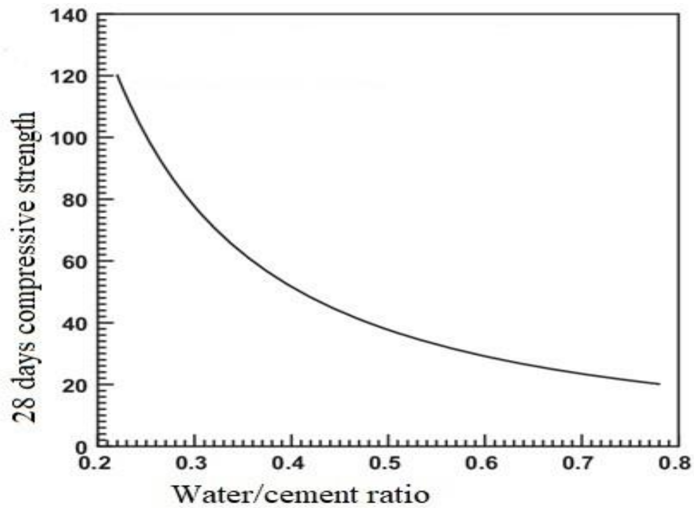

Fig. 12. The strength graphs for the water/cement ratio of standard concretes [8].

- FTIR results match the peaks in each raw material. So detailed generalization of the bond structure is appropriate.
- In the fluidity test, Mpeg5000 was observed to provide much more fluidity. The difference between the fluidity without super plasticizers and the fluidity with super plasticizers is almost 250%. After 1 percent of the expected super plasticizers for use in the test mixture has reached the saturation viscosity is not changed fluidity.
- SP polymers synthesized in the study increased the fluidity of the cement-based mixture more than twice. In order to provide the same fluidity, approximately 70% more water should be added to the cement mixture.
- In the 28-day drying period, if the super plasticizers are too inefficient, since drying starts from the outside, drying does not occur from the inside, so its strength decreases.

5. CONCLUSIONS

In the experiments by connecting a plurality of parameters when selecting the appropriate optimal values according to the appropriate product and polymerizing bond products it was synthesized.

We can say that bio raw material syntheses are encouraging in the future, with the flower oil being more resistant in the Compressive Strength test.
For this reason, super plasticizers should be placed much less and retain much more water, so their strength should be increased and their fluidity should be at an optimal level.
While the super plasticizers polymers were converted to sodium form, there was no problem in the polymers synthesized with bovine gelatin and MPEG5000. However, when adjusting the pH value of the polymer synthesized with epoxied sunflower oil-Huntpol AA, the pH value should be adjusted carefully. Otherwise, the sudden change in pH value leads to a saponification reaction.
As a result of the project, three polymeric additives were successfully synthesized, and analysis and performance tests were completed.
The only identified disadvantage of the obtained additives; is the partial removal of polymers from the drying concrete surface.

REFERENCES

[1] Liu X., Wang Z., Zheng Y., Cui S., Lan M., Li H., Zhu J., Liang X. Preparation, Characterization and Performances of Powdered Polycarboxylate Superplasticizer with Bulk Polymerization. College of Materials Science and Engineering 2014; 7: 6169-6183.

[2] Arat R. Synthesis and Characterization of New Generationpolymeric Additives for Cem I Cement Mortar, MSc, İstanbul Technical University, İstanbul, Turkey, 2010, 1-68.

[3] Hui W., Huiling G., Jiaheng L., Ronguo Z., Yong L. Research on synthesis and action mechanism of polycarboxylate superplasticizer. Front. Chem. China 2007, 2(3): 322–325.

[4] Flatt R., Schober I. Superplasticizers and the Rheology of Concrete. In Nicolas Roussel. 1 st ed. Understanding the Rheology of Concrete. Woodhead, 2012.

[5] Houst Yves F., Bowen P., Perche F., Kauppi A., Borget P., Galmiche L., Le Meins J.F., Lafuma F., Flatt R.J., Schober I. Design and Function of Novel Superplasticizers for more Durable High performance Concrete (Superplast Project). Cement and Concrete Research, 2008, 38: 1197–1209.

[6] Liu X., Guan J. Yunsheng Z., Wang Z., Ren X. Synthesis of High Performance Polycarboxylate Superplasticizer through Redox Initiation System and its Application in Concrete. College of Materials Science and Engineering, 2016, 723: 681-686.

[7] Rongguo Z., Qiong L., Anfu Z., Yong L., Jiaheng L. The Synthesis Technique of Polyacrylic Acid Superplasticizer. Journal of Wuhan University of Technology-Mater. Sci. Ed., 2008, 23, (6): 830-833.

[8] Dinakar, P., & Manu, S. N. Concrete Mix Design for High Strength Selfcompacting Concrete using Metakaolin. Materials and Design, 2014, 60: 661–668.

[9] Silvaa W., Bufalino L., Martins M., Júnior H., Tono G., Mendes L. Superabsorbent Ability Polymer to Reduce the Bulk Density of Extruded Cement Boards, Journal of Building Engineering, 2021, 43: 103130.

[10] Mechtcherine, V., Wyrzykowski, M., Schröfl, C. Application of Super Absorbent Polymers (SAP) in Concrete Construction, 2021, 54, 80.

[11] Sidiq A., Gravina R., Setunge S., Giustozzi F. The Effectiveness of Super Absorbent Polymers and Superplasticizer in Self-Healing of Cementitious Materials, Construction and Building Materials, 2020, 253: 119175.

[12] Mechtcherine, V., M. Gorges, C. Schroefl, A. Assmann, W. Brameshuber, A.N.B. Ribeiro, D. Cusson, J. Custdio, E.F. da Silva, and K. Ichimiya. Effect of Internal Curing by Using Superabsorbent Polymers (SAP) on Autogenous Shrinkage and Other Properties of a High-Performance Fine-Grained Concrete: Results of a RILEM Round-Robin Test. Materials and Structures, 2014, 47(3): 541-562.

[13] Snoeck, D. and N. De Belie. Repeated Autogenous Healing in Strain-Hardening Cementitious Composites by Using Superabsorbent Polymers. Journal of Materials in Civil Engineering, 2016, 28(1): 04015086.

[14] Cuenca, E., A. Tejedor, and L. Ferrara. A Methodology to Assess Crack-Sealing Effectiveness of Crystalline Admixtures Under Repeated Cracking-Healing Cycles. Construction and Building Materials, 2018, 179: 619-632.

[15] Abdollahnejad Z., Kheradmand M., Pacheco-Torgal F. Influence of two commercial superplasticizers and a biopolymer on the performance of waste-based alkali-activated mortars, Bio-based Materials and Biotechnologies for Eco-Efficient Construction, 2020, 43-46.

[16] Mermerdaş K., Manguri s., Nassani D., Mahdi S. Effect of aggregate properties on the mechanical and absorption characteristics of geopolymer mortar, Engineering Science and Technology an International Journal, 2017, 20:6.

[17] Salih S., Mohamed J. H. Effect of Plastic Optical Fibers on Properties of Translucent Concrete Boards, First International Conference on Engineering Sciences' Applications, ICESA, 2014, 453-466.

[18] Werani M., Lei L. Influence of side chain length of MPEG – based polycarboxylate superplasticizers on their resistance towards intercalation into clay structures, Construction and Building Materials, 2021, 281:122621.