Testing and Evaluation of Flowability, Viscosity and Long-Term Compressive Strength of Cement Modified with Polymeric Admixture WR Superplasticizer

Lajan Burhan¹, Kawan Ghafor², and Ahmed Mohammed²
¹College of Engineering, Department of Civil Engineering, University of Sulaimani, Iraq, Kurdistan Region
Email: lajan.abdalla@univsul.edu.iq, Corresponding author* Phone: 00964772331030
²College of Engineering, Department of Civil Engineering, University of Sulaimani, Iraq, Kurdistan Region

Abstract. In this study, the effect of three types of powder polymer water reducer (WR) superplasticizer on the fluidity, rheological properties, density and mechanical properties of cement were investigated. The behavior of cement paste in the liquid phase and hardened phase modified with polymers up to 0.25% (by dry weight of cement) were studied. The amount of mixing water was reduced and varied between 20% - 58%. The Vipulanandan model was used to predict the water to cement ratio (w/c) of cement. The flowability, compressive strength, and density at different curing times were increased with increasing the polymer content. Three different brand of water reducer (WR) powder polymer increased the apparent viscosity of the cement paste; the viscosity was varied between 135 cP and 652 cP based on the type of polymer, polymer content, temperature, and water to cement ratio (w/c). Using of 0.25% of polymers to the cement increased the compressive strength of the cement paste by 127% to 426% based on the types of polymer, polymer content, and water to cement ratio (w/c) and curing time. Regression analysis was used to evaluate the effect of each polymer contents, w/c and curing time on the compressive strength of cement paste.

Keywords: Water-cement-ratio, Flowability, Curing age, Polymer content, Compressive strength, Regreassion analysis.

1. Introduction
Cement, proper building materials and the primary binding agent for concrete, the most widely used durable and essential building material. Cement production has exceeded about 3.6 billion tones every year; cement industries are responsible for about 5–8% of the total worldwide CO₂ emission [1, 2, 3]. Several techniques have been used trying to replace cement, but there was no suitable and sufficient material such as cement, byproducts materials such as silica fume, fly ash, slags, metakaolin, pozzolan materials, polymer, chemical admixture, and raw materials can be used to modify cement [4-9]. Many types of research have been implemented and using different types of admixture to improve the properties of cement [10-13]. Polymers in cement composites are one of the chemical admixtures that have been used since 30th years of the 20th century. Since that time many kinds and forms of the polymers have been used in cement industry [7]. The performance of the polymer on the physical and mechanical properties of Portland cement (PC) pastes was investigated. The results presented that the polymer enhances most of the specific properties of cement such as reducing the amount of mixing water, increasing workability, retards the setting times, increasing compressive strength, decreasing drying shrinkage and permeability [9, 14, 15]. There are many types of polymer in both liquid and powder form. One of the most popular types of the polymer is Polycarboxylate (PCE) (Superplasticizer-high range water reducing) [16, 17]. Superplasticizer (High range water reducing admixtures- HRWRA) was commonly used with OPC to decrease its water content and improve the workability of the cementitious system causing in better strength and durability of concrete [19]. Water reducer (WR) defined as an admixture that decreases the volume of
mixing water for cement paste and concrete for a specified workability. Normal water reducers decrease the water to cement ratio (w/c) by 10-15%, whereas superplasticizers are efficient to reducing the water requirements by 30% or higher [15, 17]. There are several types of superplasticizers according to the chemical compositions, like lignosulphonates (Lig), naphthalene (N) and melamine-based (M), and modified Polycarboxylate (PC) [11, 19]. Superplasticizers are adsorbed on the cement particles and act as dispersants by electrostatic and steric repulsion effects on cement particles in the cement-water system [15, 17, 18]. The dispersal of cement particles is due to negative charge left on the admixture adsorbed cement particle, which will resist the other cement particles [9, 11, 16]. (Khudahir et al. 2018) [17] Studied the effect of polymer in liquid form (Polycarboxylate – superplasticizer) to develop the physical properties and mechanical performance of concrete in both fresh and solid state. Different dosage of the polymer was used ranged between 0.5% - 4% by (dry weight of cement). The compressive strength was increased by increasing the polymer content.

In this research, 3 different kinds of polymer (Polycarboxylate superplasticizer) were used to improve the properties of cement in both hardened and fresh states. The different percentage were used to modify the cement were ranged between 0 - 0.25% (by weight of cement).

2. Research Significance
The main objective of this research was to evaluate the influence of 3 different types of polymer (Polycarboxylate superplasticizer) on the flowability, viscosity, setting time and compressive strength of cement.
(i) To measure the consequence of polymers on the rheological properties of cement like flowability, viscosity, and setting times.
(ii) To measure the effect of polymers on the hardened properties of cement like density and compressive strength of cement at different curing times.
(iii) To quantify the compressive strength of cement modified with polymers as a function of curing times, w/c, polymer content and type of polymers using non-linear model (NLM).

3 Materials and methods
3.1 Materials
3.1.1 Cement. Ordinary Portland Cement (OPC) from the Gasin Cement Company was used in this study (Iraq, Kurdistan-Region, Sulaymaniyah City, 35°52′24″ N, 45°2′74″ E, Z 867m).
3.1.2 Water. Tap water was used during the test process.
3.1.3 Powder Polymers. Three types of powder polymer (Polycarboxylate superplasticizer) were used in this study. The properties of polymers are summarized in Table 1.

| Polymer Name | Polymer 1 | Polymer 2 | Polymer 3 |
|--------------|-----------|-----------|-----------|
| Product Name | Polycarboxylate Superplasticizer powder | Solid Polycarboxylate Powder | Polycarboxylate Superplasticizer |
| Appearance   | White powder | White to pale pink powder | White to yellowish powder |
| Solid Content (%) | 98 ± 1% | 97 | - |
| Bulk Density (km/m³) | 500 | 350 - 450 | ≥ 450 |
| pH Value     | 7 - 9 | 6 - 8 | 8 - 10 |
| Air Content (%) | - | - | < 2.7 |
| Chloridation (%) | < 0.1 | - | < 0.6 |
| Alkali (%)   | < 5 | - | < 5 |

3.2 Test Methods
3.2.1 Setting time (BS EN 196-3:2016). The setting times were measured by seeing the penetration of a needle into a cement paste with a standard consistency until it reaches identified value.
3.2.2 Flowability (ASTM C230). The fluidity of cement paste was measured by using the mini-slump cone test method as defined in ASTM C230. The upper, bottom diameter and the height of the cone were 70 mm, 100 mm and 60 mm respectively. The flow of cement paste for w/c of 0.5 was 154 mm.

3.2.3 Rheological test. The rheology test for cement slurry improved with three types of the polymer at different temperatures 25°C and 50°C with w/c ratio of 0.5 were tested using a viscometer. The viscometer machine was calibrated using different standard solutions. All the rheological tests were made after ten minutes of mixing [13]. The average of three sample was taken for each condition.

3.2.4 Compressive strength (CS) (ASTM C349). In this study, the prisme sample with a dimension of (40 * 40 * 160) mm was used; the rate of loading was 0.20 MPa/s in a constant rate without shocking. Average of 3 samples was tested for each condition. Moreover, the average of the three samples was recorded as the compressive strength of cement at a specific age of curing.

3.2.5 Mix proportion. The control mix was started with a w/c = 0.50, the amount of cement and water was 2000 gm and 1000 gm respectively. Different types of the polymer were replaced by dry weight of cement; polymer content was varied between 0.10% - 0.25%. Adding different polymer content reduces the amount of water required for the mix; the w/c was decreased to 0.21 based on polymer type and polymer content. Three dosage of the polymer was used for each dosage the amount of mixing water was reduced gradually.

3.2.6 Curing condition. In this study, the different curing time for the compressive strength of cement was taken into consideration, 1, 3, 7, 28 and 90 days. The samples were cured in water for the desired age of curing, and the temperature of the water was kept at 23±2°C and humidity of 95%.

3.2.7 Modeling

3.2.7.1 Comparison of Model Predictions. In order to compare the model predictions statistical quantification such as coefficient of determination (R²) and the root mean square error (RMSE) was used and quantified as follows:

\[ R^2 = \left( \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i (x_i - \bar{x})^2} \sqrt{\sum_i (y_i - \bar{y})^2}} \right)^2 \]  

\[ RMSE = \sqrt{\frac{\sum_{i=1}^{N} (y_i - \hat{y}_i)^2}{N}} \]  

Where:
- \( y_i \) = experimental value
- \( x_i \) = predicted value from the model
- \( \bar{y} \) = mean of the actual test values
- \( \bar{x} \) = mean of calculated values and N is the number of data.

3.2.7.2 Nonlinear (NLM) compressive strength model. The effect of water to cement ratio (w/c), curing time (t), and percentage of different type’s polymer on the compressive strength (\( \sigma_c \)) were investigated.

(i) The compressive strength of concrete (with 0% of additives)

\[ \sigma_c = a \left( \frac{w}{c} \right)^b (t)^c \]  

(ii) The compressive strength of concrete modified with different types of polymer (P %).

\[ \sigma_c = a \left( \frac{w}{c} \right)^b (t)^c + d \left( \frac{w}{c} \right)^e (t)^f (P)^g \]  

a, b, c, d, e, f and g are the equation variable.

4. Results and Discussion

4.1 Setting time (BS EN 196-3:2016)
The effect of polymer content and polymer type on the setting times of cement paste was presented in (Fig.1). The test results show by increasing the percentage of the polymer the initial and final setting time of cement was increased. Initial and final setting time for the control sample was 147 min and 200 min respectively, the initial setting time was increased from 155 min to 309 min according to the type of polymer and polymer content, and the final setting time was increased by 95% when 0.25% of the polymer was used. Increasing in the setting time is due to the presence of powder polymer (polycarboxylate superplasticizer) which delays the hydration of main cement composition (C3A) [19].

**Figure 1** Variation of the setting times of cement paste and polymer content (a) initial setting time and, (b) final setting time.

4.2 Flowability (mm)

Fig.2 shows the test result for the flowability of cement modified with polymers. Increasing the flowability of cement paste was due to the dispersion of agglomerate cement particle in the mix. The flowability effect of polymer (Polycarboxylate Superplasticizer) is mainly related to their adsorption onto cement surfaces.

**Figure 2** Variation in flowability of cement paste and polymer content.

4.3 Apparent viscosity (Av)

The apparent viscosity is the shear stress applied to cement slurry divided by the shear strain rate. The apparent viscosity of cement slurry with w/c of 0.5 at a shear strain rate of 170 s⁻¹ (100 rpm) at a temperature of 25°C was 103.5 cP. By changing the temperature to from 25°C to 50°C the apparent viscosity of cement slurry was increased to 165.3 cP Using different types of polymer improved the apparent viscosity of the cement slurry by 31% to 294% based on the type of polymer, water to cement ratio (w/c) and temperature (T) as shown in (Fig.3).
4.4 Water Content
The amount of mixing water was reduced by adding the different types of polymer; each polymer has a different effect on the amount of mixing water. Fig.4 presents the percent of water reducing for each type of polymer and its content. The w/c for the control mix was 0.5, and it was varied between 0.39 to 0.21 based on types of polymer, and it is content Fig.5 shows the reduction in w/c with polymer content. Moreover, w/c was correlated with the polymer dosage using Vipulandanan correlation model (Vipulanandan and Mohammed 2014) as shown in (Fig.6).

\[ w/c = 0.5 - \frac{P}{0.5 + 1.5 \times P} \]

Root mean square error (RMSE) = 0.02  \( R^2 = 0.94 \)  \( (4) \)

4.5 Density
The density of the control sample was about 1871 kg/m³, generally, by adding the different polymer dosage, the density of the cement paste was increased by 7.5% to 24% based on polymer type, polymer dosage, w/c as presented in (Fig.7). This change in density was due to the evaporation of the water in the mix. Amount of water in the control sample was more than the cement modified with polymer, So, the hydration and evaporation of water was more than the cement modified with a polymer.
4.6 Compressive strength of cement modified with the polymer (ASTM C349)

The compressive strength of cement was improved with the addition of the polymer as shown in (Fig.8). Growth in CS of cement modified with different polymer content at different curing time was presented in (Fig.9). The main reason for this improvement in compressive strength was due to reducing the amount of water required for the mix. The consequence of curing time, polymer kind and polymer dosage on CS of cement discussed in the following:

4.6.1 1 day of curing. The CS of cement at one day of curing was improved considerably ranged between 16.6 MPa to 87 MPa based of the type of polymer, w/c, and polymer dosage as shown in (Fig.8). Based on the type of polymer and polymer content the growth in CS of cement was varied between 60% to 426% as shown in (Fig.9).

4.6.2 3 days of curing. The compressive strength of cement at 3 days of curing was increased from 26 MPa to 113 MPa based on the polymer kind, w/c, and polymer dosage as presented in (Fig.8). The percentage of growth in compressive strength of cement at 3 days of curing was ranged between 82% to 336% according to polymer content, w/c and type of polymer as shown in (Fig.10). As the growth in CS for polymer 2 was varied between 93% to 336% based on polymer content as presented in (Fig.10). At 3 days of curing effect of polymer 1 and 2 was more than the polymer 3 as shown in (Fig.11).

4.6.3 7 days of curing. The CS of cement modified with the polymer at 7 days of curing was enhanced from 31 MPa to 121 MPa based on the polymer type, w/c, and polymer dosage as shown in Fig.8. The percentage of growth in compressive strength of cement modified with the polymer at 7 days of curing was ranged between 64% to 288% according to polymer content, w/c, and type of polymer as shown in Fig.9. The rate of growth in CS at 7 days of curing was reduced compared with growth in 1 day and 3 days of curing. Polymer 3 with 0.1% content was most effective in increasing the CS at different curing days of compared with the polymer 1 and 2.
4.6.4 (28) days of curing. Based on polymer type, w/c, and polymer content the CS of cement modified with the polymer at 28 days of curing was varied between 40 MPa to 135 MPa as shown in (Fig.8). The growth in CS was ranged between 61% to 235% according to type and polymer content as shown in (Fig.9). The maximum growth was polymer 2 ranged between 62% to 235%. Fig.10 shows that polymer 2 was more effective than polymer 1 and polymer 3 at 28 days of curing. The relation between the CS of cement at 28 days of curing and flowability of cement was presented in Fig.12 which is by increasing the polymer content CS, and flowability of cement was improved, and the w/c was decreased.
4.6.5 (90) days of curing. At 90 days of curing CS of cement was varied between 49 MPa to 152 MPa as shown in Fig.8 according to the kind of polymer and polymer dosage. The rate of growth in CS was decreased compared with 28 and 7 days of curing, the rate of growth was decreased because the rate of hydration decrease day after day, the growth was varied between 47% and 208% as shown in (Fig.9).

4.7 The comparison between the measured and predicted the CS of cement modified with different polymers
Regression analysis was used to study the influence of polymers dosage, water content and curing age on the CS of cement, CS of cement was predicted as a function of w/c, polymer content, and curing time up to 90 days of curing using non-linear relationship (Eq.3 (b)) as displayed in Fig.13.

4.7.1 Polymer 1 (P1). To examine the effect of polymer 1 on the CS of cement a non-linear model (Eq.3 (b)) was advanced:

$$\sigma_c = 9.4 \left( t^{0.21} w/c^{0.94} \right) + 12 \left( t^{0.03} P1^{0.2} w/c^{1.05} \right) e$$

From the nonlinear model parameter, $a = 9.4$ (Eq.5) the amount of water had the maximum effect on increasing and decreasing the CS of cement at 0% of polymer compared to the curing age. according to the nonlinear model parameter $d = 12$ (Eq.5) the w/c had the highest consequence on enhancing the compressive strength of cement compared with the polymer 1 and curing time.

4.7.2 Polymer 2 (P2). Non-linear model (Eq.3 (b)) was found to examine the effect of polymer 2 on the CS of cement.

$$\sigma_c = 9.4 \left( t^{0.21} w/c^{0.94} \right) + 15 \left( t^{0.06} P2^{0.35} w/c^{1.2} \right)$$

Based on model parameter $d = 15$ and $g = 0.35$ (Eq.6) the polymer 2 had more effect on increasing the CS of cement as compared with the polymer 1.

4.7.3 Polymer 3 (P3). A non-linear model (Eq.3 (b)) was developed to predict the CS of cement as a function of w/c, curing age, and content of polymer 3.

$$\sigma_c = 9.4 \left( t^{0.21} w/c^{0.94} \right) + 13.5 \left( t^{0.01} P3^{0.30} w/c^{0.75} \right)$$

Figure 9 Variation of growth in CS of cement paste modified with polymers at different curing age. (a) Polymer 1, (b) Polymer 2, and (3) Polymer 3

Figure 10 Comparison between CS of cement modified with polymer at 3 days of curing

Figure 11 Comparison between CS of cement modified with polymer at 28 days of curing

Figure 12 Relationship between the flowability and CS of cement paste using different types of polymer
According to the nonlinear model parameter $d = 13.5$ (Eq.7), the content of polymer 3 had more influence on the CS of cement compared to the curing age. From nonlinear model parameter, $d = 12, 15, \text{and } 13.5$ for polymer 1, 2, and 3 respectively, polymer 2 had the maximum outcome on the CS of cement compared to polymer 1 and 3.

5. Conclusions

Different types of polymer had a specific effect on the plastic and mechanical properties of cement paste in both fresh and hardened state. Different types of polymer reduce the amount of water required for mixing and w/c. Setting times of cement and flowability of cement improved by using a different amount of polymer. The main conclusion of this study was as follows:
1- Initial and final setting time of cement paste increased with increasing different amount of polymers, because of the presence the (Polycarboxylate superplasticizer) delay the hydration of C3A.
2- The apparent viscosity of the cement paste was increased by using different types and amount of polymer, by increasing the temperature from 25℃ to 50℃ the viscosity also increased.
3- The density of hardened cement paste was increased by using different polymers because the amount of mixing water was reduced.
4- The compressive strength of cement paste modified with polymer was increased by 336% at an early age when 0.25% of the polymer was replaced by weight of cement.
5- The rate of growth in compressive strength for polymers at an early age (3 days of curing) much higher than the 7, 28 and 90 days of curing.
6- Compressive strength was predicted well as a function of w/c, curing time, different type of polymer. From the NLM parameter effect of polymer type and amount on the increasing and decreasing the compressive strength of cement paste was different depending on the type of polymer.
7- The optimum dosage of the polymer to enhance the cement properties was 0.25%.
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