Evaluation and nonlinear quantification of early age strength of concrete containing PCE polymer

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Abstract This research is focused on the impact of three types of polycarboxylate polymer (PCE) on the plastic properties such as setting time of cement and slump of concrete and also, to assess their effects on compressive strength (CS) and concrete density. The percentage of each type of polymer ranged from 0 to 0.25% (by weight of cement). The slump test and CS results of concrete modified with polymers were compared with the silica fume concrete used in the literature. The water to cement ratio (w/c) initially was 0.60 and decreased gradually to 0.46 by increasing the polymer dosage. The CS of concrete modified with 0.25% of polymers increased by 24% and 97% based on the polymer type, polymer content, w/c and curing age. Non-linear regression analysis was used to model the compressive strength of concrete modified with three types of the polymer as a function of polymer content, w/c, and curing time. Based on the literature data and results of this study, it found that the polymers are more effective than silica fume on enhancing the workability and CS of concrete.

Keywords
Water to cement ratio, Workability, Curing time, Polymer content, Compressive strength, Modelling.

1. Introduction
Concrete is a construction material used for various types of structure due to the structural stability and strength [1]. Concrete is a suitable construction material with many applications and it has many excellent properties, such as good compressive strength, and excellent durability and stiffness, low cost, and ease of fabrication. Many techniques were used to improve the concrete property and modify the undesirable property to desirable features can be modified using admixture, pozzolanic materials, different types of aggregates, various water-cement ratio, and different types of polymers (Polycarboxylate - superplasticizer) [2]. Different cementitious materials were used to develop the mechanical behavior of concrete, such as fly ash, and silica fume. Pozzolanic materials usually are capable to combine with the hydrated calcium hydroxide (Ca(OH)$_2$) to form the hydrated calcium silicate (CSH-gel)[3, 4, 5]. Zain et al. [6] used 10% of SF as a cement replacement to enhance the CS of concrete, with different w/c ranged between 0.40 to 0.50. The CS of concrete modified with silica fume increased by 9% at 28 days of curing. Dotta et al. [3] studied the influence of SF on the physical properties of concrete; the SF content was between 6% and 12% by dry weight of cement; the w/c was varied between 0.65 and 0.50. The maximum growth in CS at 28 days obtained was 35% as compared with no SF concrete. An undesirable impact of SF on the workability of fresh concrete was noted. The workability of the control sample was 50 mm, and by adding 1% and 2% of silica fume, the workability was decreased to 30 mm and 20 mm respectively [7].

The polymer is one of the chemical admixtures that used to improve the properties of concrete in both fresh and hardened states. Polymers affect the setting times, bleeding, workability, hydration and properties of cement [8]. There are many types of polymer in both liquid and powder form. One of the most common types of polymer is Polycarboxylate (PCE) (Superplasticizer-high range water reducing)
In latest years, the invention and manufacturing of concrete admixtures have developed quickly with a propensity to make high strength and high-performance concrete. Polycarboxylate superplasticizer (PCE) or high range water reducers have become one of the essential admixtures for concrete [10, 11]. Normal water reducers decrease the w/c by 10 to 15%, while superplasticizers are capable of decreasing the water content by 30% or higher [8, 9, 12, 13, 14]. At present, most existing superplasticizers, based on the chemical composite, can be classified into four main groups. The first one sulphonate naphthalene formaldehyde condensate (SNF), second sulphonate melamine formaldehyde condensate (SMF), modified lignosulphonate (MLS) belong to the third group and the last group copolymers containing sulphonic and carboxyl groups like the Polycarboxylate-type superplasticizers (PC). The workability of fresh concrete and durability of concrete could be developed significantly using PC superplasticizers [8, 15, 16]. The positive action of superplasticizers is because of the adsorption and dispersion of the cement grains in the cement-water system [8, 9]. The adsorption of superplasticizers is a key factor for the invention of low water content concrete [17]. Dispersion of conglomerate cement particles is known to be the main factor by which superplasticizers develop the workability of fresh concrete. A significant factor is to ensure that the polymer adsorbs onto the cement particle and has a configuration which maximizes its capacity to disperse agglomerated particles [17, 18]. In this research, three different kinds of polymer (Polycarboxylate superplasticizer) were used to improve the quality of concrete in both hardened and fresh states. Different percentages were used between 0 to 0.25% (by weight of cement).

The general aim of this research was to evaluate the influence of three different kinds of polymer (Polycarboxylate superplasticizer) on the workability and CS of concrete, and the results were compared with concrete modified with SF used in the literature. The specific objectives are as follows:

(i) To find the effect of polymers on the setting times of cement, workability of fresh concrete, and density of hardened concrete.

(ii) To examine and measure the impact of polymers on the CS of normal strength concrete at the early age of curing.

(iii) To quantify the compressive strength of concrete modified with polymers as a function of curing times, w/c, polymer content and type of polymers using NLM.

2. Materials and methods
2.1. Materials
2.1.1 Cement. Ordinary Portland Cement (OPC) from the Gasin Cement Company was used for this study. The chemical composition listed in the table 1 below.

| Chemical composition | Chemical formula | Chemical content (%) |
|----------------------|------------------|----------------------|
| Lime                 | CaO              | 63.9                 |
| Silica               | SiO₂             | 20.1                 |
| Alumina              | Al₂O₃            | 4.08                 |
| Ferrite              | Fe₂O₃            | 5.10                 |
| Magnesia             | MgO              | 1.48                 |
| Sulfur trioxide      | SO₃              | 2.20                 |
| Loss on Ignition     | LOI              | 3.41                 |

2.1.2 Fine Aggregate (Sand). Crushed sand from (Tanjaro in the south-west of Sulaymaniyah City, 35°47'61" N, 45°43'31" E, Z 668m), was used in this study with a bulk specific gravity of 2.51 according
to ASTM 128-15 specification. Percent of absorption and fineness modulus were 2.25% 2.79 according to ASTM 136M-14 specification. Gradation for fine aggregate confirms ASTM C33 standard specification.

2.1.3 Coarse Aggregate (Gravel). Crushed gravel from Tanjaro in the south-west of Sulaymaniyah city, was used with maximum size of 25 mm, bulk specific gravity 2.28, and water absorption 1% according to ASTM C127-15 specification. The gradation also confirms ASTM C33 specification for fine and coarse aggregates.

2.1.4 Water. Tap water was used for both mixing and curing process.

2.1.5 Polymers. Three types of powder polymer (Polycarboxylate superplasticizer) were used in this study. The names of the three polymers in the current study are (PCE1), (PCE2), and (PCE3), the properties of each type of polymer are given in the table 2.

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

2.2. Test Methods

2.2.1. Setting time test (BS EN 196-3:2016). The setting time was determined using vicat apparatus by noting the penetration of a needle into cement with a standard consistency until it reaches 5 mm to 7 mm from bottom of vicat mold.

2.2.2 Measurement of Slump (ASTM C143) and (EN-12350). Concrete slump test was used to measure the workability of concrete and to determine the effect of polymers on the workability of fresh concrete mix.

2.2.3 Compressive strength (EN-12390-3). In this study, the cube sample with a side of 150 mm was used; the rate of loading was 0.6 MPa/s in a constant rate without shocking. Three samples were tested for each age of curing and polymer content. And the average of the three samples was recorded as strength of concrete at a specific age of curing.

2.3 Mix proportion.
The control mix was designed according to ACI-211.1-91 for normal strength concrete; the concrete mix is designed to have a CS of 21 MPa at 28 days of curing. Based on the ACI-0211, the w/c of the control sample was 0.60. The polymer contents were varied between 0% to 0.25%. The addition of the
polymer cause a reduction in the amount of mixing water, and the w/c was reduced gradually in such a way the slump value remains more than the control sample.

2.4 Curing condition.
In this study, three different curing times for the CS of concrete were taken into consideration, 3, 7 and 28 days. The samples were cured in water for the desired age of curing, and the temperature of the water was kept at 25±2°C and humidity of 95%.

3. Modeling

3.1 Nonlinear compressive strength models
The effect of water to cement ratio (w/c), curing time (t), and percentage of different categories of polymer on the CS ($\sigma_c$) were investigated:

(i) The CS of concrete (with 0% of additives)
$$\sigma_c = a \left( \frac{w}{c} \right)^b (t)^c$$

(ii) The CS of concrete modified with three various brands of polymer (P %).
$$\sigma_c = a \left( \frac{w}{c} \right)^b (t)^c + d \left( \frac{w}{c} \right)^e (t)^f (P)^g$$

Based on experimental data model parameters (a, b, c, d, e, f, and g) were obtained from multiple regression.

4. Results and Discussion

4.1 Setting time (BS EN 196-3:2016)
Figure 1 shows the effect of each polymer on the initial and final setting of cement paste. The test results show by increasing the percentage of the polymer the initial and final setting time of cement was increased. Increasing in the setting time is due to the presence of powder polymer (polycarboxylate superplasticizer) which delay the hydration of C3A in cement which is one of the main components in cement [8].

![Figure 1. Variation of the setting times of cement paste and polymer content (a) initial setting time and, (b) final setting time](image-url)
4.2 Slump test (ASTM C143) and (EN-12350)
The slump of the control mix was 125 mm, and the range of the slump for all the concrete modified with polymer were ranged between 125–150 mm, by increasing the polymer content the slump and viscosity of concrete were increased. The effect of different types of the polymer at a different percentage of polymer on the workability of fresh concrete (Figure 2). The comparison between the effect of silica fume and the polymers on the slump with CS are presented in Figure6. Based on the data collected from literature silica fume reducing the workability of fresh concrete, which by increasing the CS the slump or workability of fresh concrete was decreased considerably in (Figure3). Patil et al. [21] used the different percentage of silica fume to improve the CS of concrete from 25MPa to 35MPa, and the workability of mix was reduced from 75mm to 35mm.

4.3 Compressive strength of concrete modified with the polymers (EN-12390-3)
Figure4 shows the effect of polymer on the CS of concrete. The CS of concrete was enhanced with the addition of the polymer. The main reason for this improvement in CS was due to reducing the amount of water required for the mix. The effect of curing time, polymer type and polymer content on CS of concrete discussed in the sub sections:
Figure 4. Relationship between polymer content and compressive strength of concrete at different curing times (a) polymer 1, (b) polymer 2, and (c) polymer 3

4.3.1 3 days of curing. The CS of concrete at 3 days of curing was increased from 21 MPa to 38.6 MPa according to the type of polymer, w/c, and polymer content (Figure 4). The percentage of growth in CS of concrete at 3 days of curing was ranged between 28% to 97% (Figure 5). The increase in compressive strength for polymer 2 was varied between 57% to 97% based on polymer content and w/c (Figure 6).

Figure 5. Comparison between changes in CS of concrete modified with three types of polymer at 3 days of curing
Figure 6. Variation of the percentages of increase in the compressive strength of concrete modified with three types of polymer at three different curing times (a) polymer 1, (b) polymer 2, and (c) polymer 3.

4.3.2 28 days of curing. The compressive strength of concrete modified with the polymer at 28 days of curing was varying between 34 MPa to 50 MPa based on polymer content, w/c, and polymer type. The rate of growth in CS was less than the rate of growth at 3 days of curing. The growth in compressive strength was found between 21% to 45% according to type and polymer content as shown in (Figure 6). The maximum growth was polymer 2 ranged between 26% to 45%, and the minimum growth was polymer 1 the rate of growth was ranged between 21% to 24% based on polymer content. The effect of different polymers was compared with the effect of different percentage of silica fume on the compressive strength that used in the literature as shown in (Figure 7).

Figure 7. Comparison between growths in compressive strength of concrete modified with polymers and silica fume at 28 days of curing. [3,6,23,24,25]
Silica fume was replaced by dry weight of cement 10% at w/c of 0.46 and the growth in CS was 24% [23]. Ahmad [24] studied the effect of different percentage of silica fume ranged between 0% to 30% on the CS of concrete, the strength reduced by 10% to 18% after 28 days of curing.

Figure 7 shows the comparison between the effect of 0.25% of polymer 1, 2, 3 and silica fume ranged between 5% to 25% on the CS of concrete at 28 days of curing, the effect of only 0.25% of polymer on increasing the CS of concrete was more than the silica fume at the same w/c. The effect of various water-soluble polymers on concrete properties, it was detected that the less molecular weight polymers were more effective dispersants [8].

4.4 Water/cement ratio, (w/c)
The amount of mixing water was reduced by adding the polymers; each polymer has a different effect on the amount of mixing water, and in general, by increasing the polymer content the w/c was reduced. Figure 8 presents the amount of water reducing for each type of polymer with different percentage of the polymer (P %). Moreover, water to cement ratio (w/c) was correlated with the dosage of each polymer using Vipulandanan correlation model [26].

\[
\frac{w}{c} = 0.6 - \frac{P(\%)}{3.48 + 6.1 \times P(\%)} \quad \text{RMSE} = 0.01 \quad R^2 = 0.85
\]  

4.5 Density
The density of the control sample was 2348 kg/m³, generally, addition of different polymer contents, the density of the concrete was increased, by only 0.75% to 3% according to the type of polymer, polymer content, w/c and curing time. The density was increased because the amount of mixing water reduced and the amount of reduced water repalced by the sand and gravel to achieved the constant weight of the mix, another reason by reducing water the evaporation of water in the mix was less so the density was increased (Figure 9).

4.6 The comparison between the measured and predicted CS of concrete modified with different polymers
Regression investigation was used to study the effect of polymers content, w/c and curing age on the CS concrete, the CS of concrete was predicted as a function of w/c, polymer content, and curing age up to 28 days using non-linear relationship (Eq.1 (b)) as presented in figure 10. The model parameters were achieved from multiple regression analysis using the least square method as summarized in Table 2. The
result of the different types of polymer was compared with the effect of silica fume on the CS of concrete.

4.6.1 Polymer 1 (PCE 1). In order to investigate the effect of polymer 1 on the CS of concrete a non-linear model (Eq.3) was developed:

\[
\sigma_c = 18.5 \left( \frac{t^{0.19}}{w/c^{0.02}} \right) + 19.5 \left( \frac{w/c^{0.05} \cdot p_{2.045}^{0.94}}{w/c^{0.02}} \right)
\]  

(3)

From the model parameter \(a = 18.5\) (Eq.3) the curing time had the maximum effect on growing and decreasing the CS of concrete at 0% of additive compared to the w/c. Based on the nonlinear model parameter \(d = 19.5\) (Eq.3) the polymer 1 had the highest effect on enhancing the CS of concrete compared with the w/c and curing time.

**Figure 10.** Comparison between measured and predicted compressive strength of concrete modified with polymers.

4.6.2 Polymer 2 (PCE 2). Non-linear model (Eq.4) was found to investigate the effect of polymer 2 on the CS of concrete.

\[
\sigma_c = 18.5 \left( \frac{t^{0.19}}{w/c^{0.02}} \right) + 40 \left( \frac{w/c^{0.05} \cdot p_{2.045}^{0.94}}{w/c^{0.02}} \right)
\]  

(4)

According to parameter \(d = 40\) and \(g = 0.94\) (Eq.6) the polymer 2 had the extreme effect on increasing the CS of concrete as compared with the w/c and curing time. By comparing the parameter \(d\) in Eq.4 and Eq.6, \(d = 19.5\) and \(d = 40\) respectively shows that the polymer 2 much effective than the polymer 1 in increasing the compressive strength of concrete.

4.6.3 Polymer 3 (PCE 3). A non-linear model (Eq.5) was developed to predict the CS of concrete as a function of w/c, curing time, and content of polymer 3.
According to the nonlinear model parameter \( d = 27 \) (Eq. 5), the content of polymer 3 had the highest effect on the CS of concrete compared to the w/c and curing time. From nonlinear model parameter \( d = 27, 40, \) and 19.5 for polymer 3, 2, and 1 respectively, polymer 2 had the highest effect on the CS of concrete compared to polymer 3 and 1.

\[
\sigma_c = 18.5 \left( \frac{t^{0.19}}{w/c^{0.02}} \right) + 27 \left( \frac{t^{0.06}p^{0.69}}{w/c^{0.06}} \right) \quad (5)
\]

5. Conclusions
Different types of polymer had a particular effect on the plastic and hardening properties of cement and concrete. Different types of polymer reduce the amount of water required for mixing and w/c. Setting times of cement and workability of concrete improved by using a different amount of polymer. The main conclusions of this study were as followings:

1- The w/c of the modified concrete with polymers reduced by using different type and amount of polymers. Initial and final setting time of cement paste increased with increasing different amount of polymers.

2- By comparing the effect of different polymer and silica fume on concrete properties, the CS and workability of concrete modified with different types of polymer (up to 0.25%) was much higher than the concrete modified with different amount of silica fume (up to 25%).

3- The CS of concrete modified with polymer was increased by 97% at an early age when 0.25% of the polymer was replaced by dry weight of cement. At 28 days of curing effect of different polymer on increasing the CS was compared with effect of silica fume, growth in CS of concrete modified with different polymers was varied between 24% to 45% while the increase in compressive strength for concrete modified with different percentage of silica fume was varying between 7% to 34%.

4- Compressive strength of the concrete modified with different types of polymer was predicted well as a function of w/c, curing time, different type of polymer. From the non-linear model parameter effect of polymer type and amount on the increasing and decreasing the CS of concrete much higher than the effect of w/c and curing time.

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