

The effect of Isoprenyl Ether polymer molecular structure on cementitious composites

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ABSTRACT – In order to minimize the rapid flow loss issue from the hot weather or during lengthy periods and long-distance transport, the synthesis of the isoprenyl oxy polyethylene ether (T-PEG) was introduced. However, there were scarce amount of reported literature on the influence of main and side chain densities on the fresh and hardened properties of concrete containing T-PEG polymers. This study was conducted to investigate fresh and mechanical properties of cementitious composites containing T-PEG polymers with different main and side chain densities. These T-PEG polymers were comprised of the density ratio of side chain to main chain of 1:1, 1:1.5, 1:2, 1:2.5 and 1:3.5, respectively. The laboratory tests conducted were marsh cone funnel test, standard consistency, flow retention, flexural strength and compressive strength test. The results obtained showed that the increased density ratio of side chain to main chain of T-PEG improves the fluidity of the cement paste and the flow retention ability of the cement mortar. Consequently, the mortar with T2 polymer proved a better performance on mechanical strength tests. In conclusion, the increasing main to side chain densities ratio of T-PEG polymer imposes a significant influence on the fresh and hardened properties of the concrete material produced.

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INTRODUCTION

Generally, the polycarboxylate ether (PCE) polymers were invented to act as a water-reducing agent for either mortar or concrete applications [1–3]. Most PCE is commonly comb-shaped with an anionic backbone to generate an electrostatic repulsion with Ca^{2+} released through cement hydration [4–6]. At the same time, the polymer side chain was used to induce steric hindrance among adsorbed layers to prevent agglomeration of cement particles [7–9]. Initially, the first type of PCE was known as α -methoxy- ω -hydroxy-poly(ethylene glycol) (M-PEG), which synthesized a mixture of methacrylic acid (MAA) and poly(ethylene glycol) methyl ether methacrylate solutions (PEG). It was commonly used to improve the fluidity of the concrete by lowering the water-binder ratio while reducing the effects of segregation and bleeding in the initial stages of mixing [10–12]. However, there could be a large difference in the fluidity of the mixture caused by the rapid workability loss of the mixture. This is especially true in hot weather or during long-term and long-distance transport [13]. Besides it is one of the way to improve concrete quality in order to reduce issues for building structures [14–17].

For this, the poor flow retaining ability for this kind of PCE can be improved by adding other flow retaining agents [18–20]. However, other obstacles have been built up in terms of flowability; such as uncontrolled setting and incompatibility of cement-admixtures [18]. Consequently, another type of PCE polymer, isoprenyl oxy polyethylene ether (T-PEG), was designed and synthesized for better dispersion and flow retention abilities [18, 19, 21]. It was synthesized using isoprenyl oxy polyethylene ether (T-PEG) and acrylic acid (AA) through free radical polymerization with sodium persulfate [22, 23] or potassium persulfate [24–26] as an initiator. Moreover, it was reported that a faster spreading effect was obtained at a lower water content using acrylic or maleic acid instead of methacrylic acid [22]. This made it easier to pump into a congested formwork and higher levels of the buildings. However, this kind of PCE polymer possessed different effects in the cement performance and hydration with different molecular structures of the PCE polymer [5].

For the M-PEG, the methyl group from the MAA is substituted on the backbone of the polymer to enhance the hydrophobicity of the PCE polymer. This, in turn, improves the backbone stiffness [19]. Therefore, the backbone stiffness and hydrophobicity in T-PEG showed variation as the MAA was replaced by AA. However, a very limited amount of knowledge has been established regarding molecular structure of T-PEG polymer on fresh properties and mechanical performance of cementitious composites. Therefore, this work was focused to investigate both fresh and mechanical properties of cementitious composites containing T-PEG polymers with different main and side chain densities. At first, T-PEG polymer were prepared and synthesized through free radical polymerization, with different densities of main and side chain. It was referred to the ratio of T-PEG and AA used. Then, the fresh properties of cementitious mixture were

determined by marsh cone funnel test, standard consistency test and flow retention test. The mechanical performance of cementitious mixture was examined by both flexural strength and compressive strength.

MATERIALS AND METHODS

Ordinary Portland Cement (OPC)

The OPC was supplied by Cement Industries of Malaysia Berhad. It was in compliance to MS EN 197-1:2014 requirement under CEM I 42.5 and CEM I 52.5N. The specific surface area was 4 400 cm²/g with a specific gravity of 3.15. The chemical composition of the OPC was as shown in Table 1.

Table 1. The chemical composition of the OPC.

Chemical Compound	% by Total Mass
SiO ₂	19.06
TiO ₂	0.24
Al ₂ O ₃	4.37
Fe ₂ O ₃	3.93
MnO	0.05
MgO	0.90
CaO	54.46
Na ₂ O	0.05
K ₂ O	0.94
P ₂ O ₅	0.10
SO ₃	4.02
Loss of Ignition (%)	2.53

T-PEG type PCEs

For this study, the T-PEG was synthesized in the laboratory with the isoprenyl oxy polyethylene ether (T-PEG) and acrylic acid (AA) through a free radical copolymerization mechanism. Firstly, 20.00 g of T-PEG monomer was dissolved in 80.00 g of distilled water followed by adding 0.95 g of ammonium persulfate into the particular solution. Next, the solution was heated to 55 °C for 3 hours. Meanwhile, the respective amount of acrylic acid was added every 30 min over the heating period. The reaction mixture was then allowed to heat further for another 1 hour at 55 °C. Following the complete reaction the polymer solution was allowed to cool to room temperature and neutralized by an alkali solution of sodium hydroxide. The concentration of the final product was 25 wt % in aqueous solution with a pH of 7 ± 1. Table 2 marked the design of the T-PEG polymer. The molar ratio of T-PEG and AA was referred as the density ratio of side chain to main chain.

Table 2. The design of T-PEG polymers.

T-PEG Polymer	Molar ratio of monomer		Density ratio of side chain to main chain
	T-PEG	AA	
T1	1	1	1:1
T1.5	1	1.5	1:1.5
T2	1	2	1:2
T2.5	1	2.5	1:2.5
T3.5	1	3.5	1:3.5

Aggregate

River sand with a specific gravity of 2.63 was locally sourced to be used as fine aggregate in the mortar mixture. The sand was first washed to remove the unwanted residue then passed through a 5.0 mm sieve before dried to a saturated surface dry (SSD) condition [27].

Marsh Cone Funnel Test

The marsh cone funnel test is the simplest approach to determine rheological behavior of cementitious mixture for quality control [28]. This test was required to be conducted in accordance with ASTM C 939: 2016 [29]. Table 3 shows the mix design for the paste mixture in a 1 liter volume. The paste mixture was prepared from weighing the cement required in a mixing bowl. Next, 80 % of the water from the mix design calculation was added to the cement and mixed at high speed for 2 minutes. Then, a 0.60 % dosage of the chemical (T-PEG polymer) by binder-mass was added into the

mixture and mixed for 1 minute before adding the remaining 20 % water for 1 minute respectively. Before pouring the paste into the flow cone, the internal surface of the flow cone was moistened with water and the outlet of the discharged tube was closed with a stopper. The paste mixture was then poured into the marsh cone funnel. Finally, the stopper was removed to allow the paste mixture to flow through the flow funnel. A stopwatch was used to record the flow time.

Table 3. The mix design for the paste mixture in a volume of 1 litre.

W/C	OPC (kg/l)	Water (kg/l)	Chemical (g/l)
0.30	1.62	0.486	9.72
0.35	1.50	0.524	9.00
0.40	1.39	0.558	8.34
0.45	1.30	0.586	7.80
0.50	1.22	0.612	7.32

W/C: Water-Cement Ratio

$$W/C = \frac{\text{Weight of Water Used}}{\text{Weight of Cement Used}}$$

Standard Consistency Test

The standard consistency of the paste is well-performed to determine the amount of water content that is to be added in cement to attain normal consistency of cement [30]. This test was carried out by referring to the testing methods specified in BS EN 196-3: 2016 [31]. Firstly, the respective amount of OPC was mixed with 80 % of the mixing water for 2 minutes. Secondly, the T-PEG polymer (0.6 % by binder mass) and the remaining water was added to the mixture and mixed with high speed for another 1 minute, respectively. Then, the paste was transferred into the standard consistency mould without any compaction and vibration but removing the excess part to obtain a smooth upper surface. The paste was left for 4 minutes at room temperature before calibrating the Vicat apparatus with the plunger to obtain the resistance to penetration. The consistency was repeated with different water-cement ratio until the plunger of the Vicat apparatus penetrate into 6 ± 1 mm above the bottom of the mould. Thereby, Table 4 summarizes the mix design of the cement paste in a volume of 1 litre for this particular test. Figure 1 showed the setup of the standard consistency test.

Table 4. The mix design for the paste mixture in a volume of 1 litre.

W/C	OPC (kg/l)	Water (kg/l)	Chemical (g/l)
0.27	1.00	0.270	6.00
0.28	1.00	0.280	6.00
0.29	1.00	0.290	6.00
0.30	1.00	0.300	6.00
0.31	1.00	0.310	6.00

W/C: Water-Cement Ratio

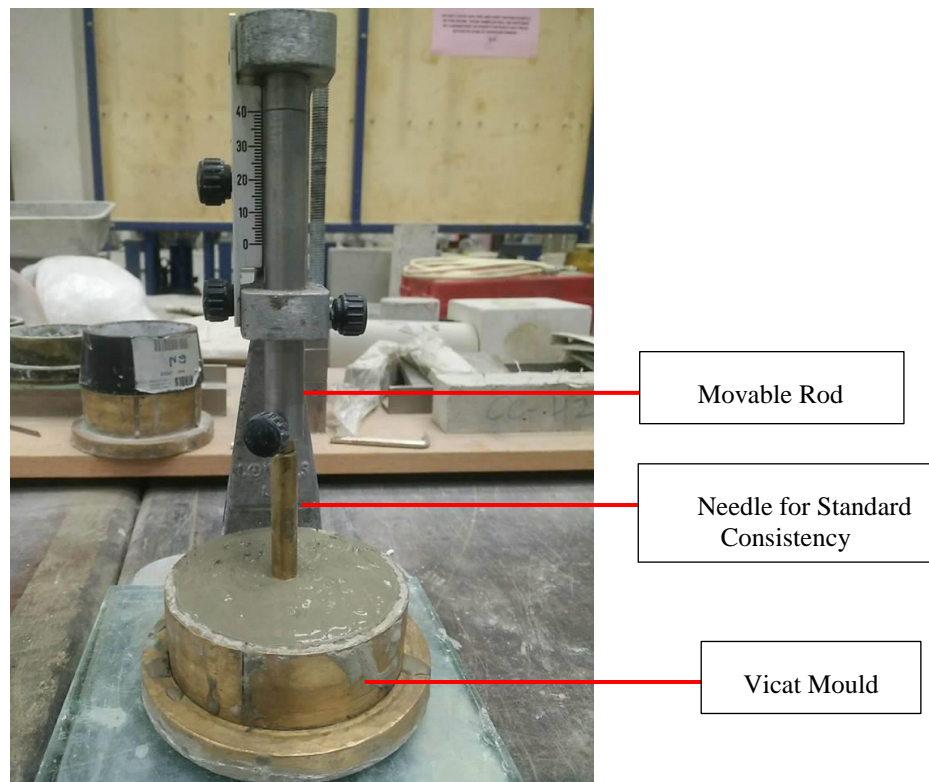


Figure 1. The setup for standard consistency test.

Flow Retention Test and Mechanical Test

Flow retention test is an important guideline to measure the workability consistency of the cementitious mixture before it sets. Meanwhile, it is useful to determine the reduction in slump or flow from the casting time to the sites. Besides, both flexural and compressive strength was necessary to determine mechanical performance of cementitious materials.

A mortar mixture was prepared for the flow retention and followed by a mechanical test in terms of flexural and compression strength. Therefore, the mix design of mortar mixture for 1 m³ volume of the material was calculated by an absolute method and tabulated in Table 5. For the mixing procedure, cement and sand was dry-mixed at low speed for at least 10 minutes to reach a homogeneous condition. Next, 80 % of the water from the mix design calculation was added into the mixture and mixed at high speed for 2 minutes. Then, a 0.60 % dosage of the chemical admixture (T-PEG polymer) was added into the mixture and mixed for 1 minute before adding the remaining 20 % water for another 1 minute respectively. The mortar flow was tested until 200 ± 5 mm of the mortar flow could be obtained by adjusting the additional water volume. Therefore, a portion of the mortar mixture was used for test flow retention while the remaining was cast into particular molds for flexural and compressive strength tests. Likewise, additional mortar has been cast without any chemical polymers added and denoted as a reference for comparison purposes. Both flexural and compressive strength tests were tested in accordance with testing methods specified in ASTM C 348: 2018 and ASTM C 349: 2018, respectively [14, 32, 33].

Table 5. The mix design of mortar mixture for 1 m³ volume of the material.

Mix Design	OPC (kg/m ³)	Sand (kg/m ³)	Water (kg/m ³)	Chemical (kg/m ³)	Water-Cement Ratio
Reference	601	1291	319	3.6	0.53
T1	601	1401	277	3.6	0.46
T1.5	601	1354	295	3.6	0.49
T2	601	1448	259	3.6	0.43
T2.5	601	1448	259	3.6	0.43
T3.5	601	1369	289	3.6	0.48

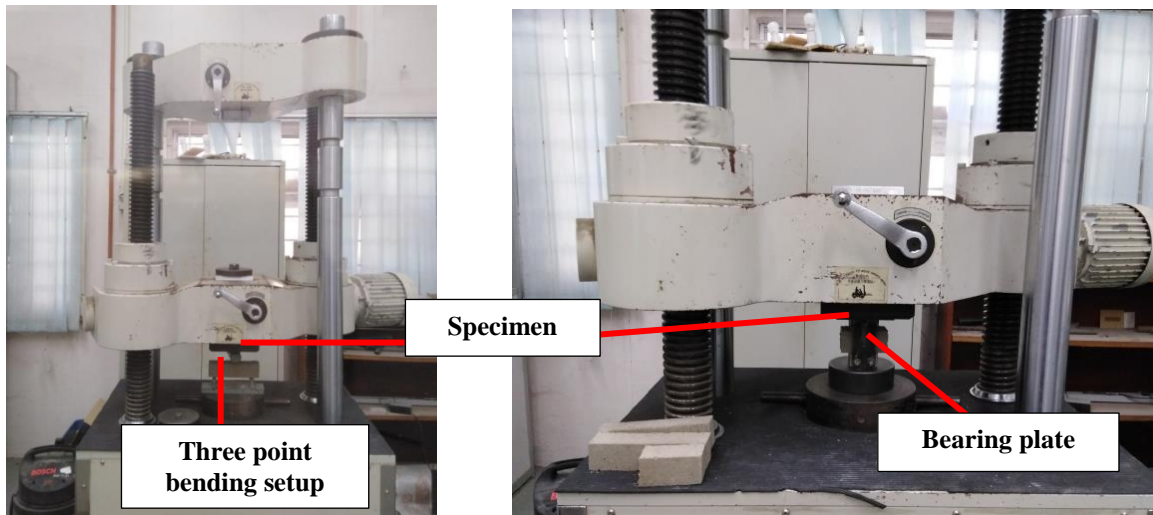


Figure 2. The setup for flexural strength test (left) and compressive strength test (right).

RESULTS AND DISCUSSIONS

Marsh Cone Funnel Test

Table 6 shows the flow time needed for 150 ml paste volume to flow through a standard marsh cone funnel to determine the fluidity of the cement paste. Most of them were not able to flow through with a W/C ratio of 0.30 but only T3.5 was able to flow through at 165 seconds duration. T1 was not able to flow through the marsh cone funnel at the W/C ratio of 0.30 and 0.35 respectively. Consequently, a bleeding effect was observed when the W/C ratio of cement paste was increased up to 0.40.

Table 6. The flow time needed for 150 ml paste volume to flow through marsh funnel.

W/C	0.30	0.35	0.40	0.45	0.50
	Flow time (s)				
T1	NF	NF	72	22	11
T1.5	NF	80	22	16	13
T2	NF	97	42	21	13
T2.5	NF	38	17	13	10
T3.5	165	51	21	--	--

*W/C: Water-Cement Ratio
NF: Not flowable*

For this, the overall results showed that the fluidity of cement paste was improved with the polymer consisting of higher carboxyl groups (higher density of side chain to main chain), with an exception of T3.5 polymer. This may be due to the fact that the dispersing action was improved when the polymer released a higher COO^- and attracted the Ca^{2+} on the cement surface through electrostatic interaction [4, 19, 34]. Therefore, the polymer adsorption layers were denser [11]. This was in good agreement with prior studies which stated that a higher charge density enhanced admixtures and mineral surface interactions, which promoted cement grain adsorption [35, 36]. At the same time, it creates more hydrogen bonds between oxygen atoms of ether bonds and water molecules [10, 37], facilitating calcium chelate complexation to provide better fluidity [5, 18, 38].

However, the paste with T3.5 polymer required a longer reaction time compared to the paste with T2.5 polymer. As mentioned, PCE side chain played an important role to induce steric hindrance effect and facilitate cement particles distribution [5]. The scarcity of polyethylene oxide (PEO) side chain in T3.5 polymer limits steric hindrance effect [8], [36]. Thus, the cement particles in the paste with T3.5 polymer were not well dispersed. In addition, an agglomeration effect tends to occur on the cement particles in this mixture, which reduced cement particles distribution [5].

Therefore, the paste with T2.5 polymer used the shortest time to complete the flow test with a varied W/C ratio. It can be concluded that the fluidity of the cement paste can be improved with an optimum grafting density of the main chain to exert a balanced effect of electrostatic repulsion and steric hindrance [39].

Standard Consistency Test

Figure 3 shows the standard consistency level of the cement paste with various T-PEG polymers, including the cement paste without chemical polymer as the reference. The results indicated that T-PEG polymer T1, T1.5, T2, T2.5 and T3.5 were effective as cement dispersant. This is because the mortar with these polymers required a lower W/C ratio than reference mortar. A W/C ratio of 0.31 was requested for the reference cement paste to achieve the level of standard consistency. The W/C ratio was reduced to 0.30, 0.29 and 0.28 for the cement paste with T1, T1.5 and T2, respectively. However, the W/C ratio was increased again to 0.29 and 0.30 for the corresponding cement paste with T2.5 and T3.5. It means that the highest amount of water was requested for the reference cement paste to reach the requirement for standard consistency.

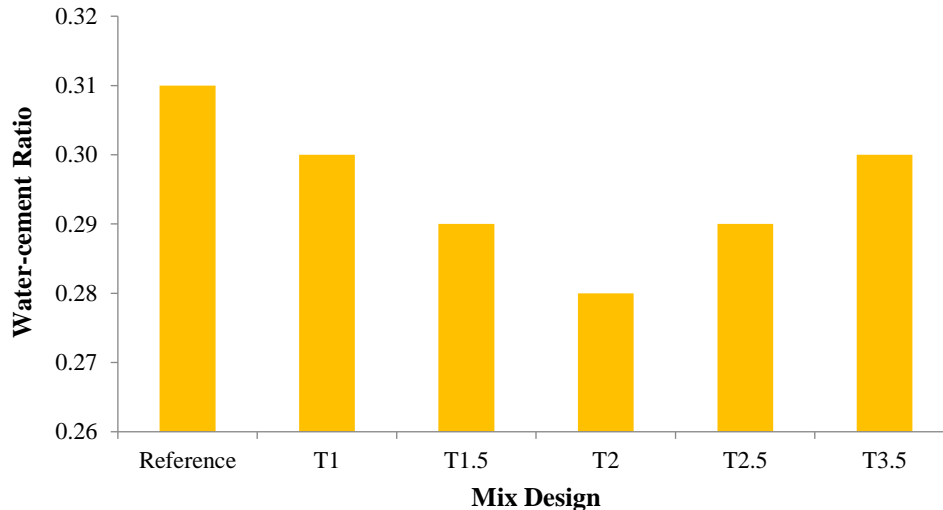


Figure 3. The standard consistency level for the cement paste with various T-PEG polymers.

Initially, calcium ions and hydroxide ions were dissociated in cement solution when mixing water was added to cement mixture [1]. When T-PEG polymer was started to add into cementitious mixture, carboxyl ions were formed subsequently [40, 41]. Meanwhile, a strong dispersion effect was created to bring towards the formation of the complexes between Ca^{2+} ion and these T-PEG polymers [18, 35]. With this theory, there were more free water molecules to be entrapped within cement particles [42–44], while reducing required water for reaching standard consistency level. Thus, the water demand was lowered for the cement paste with any T-PEG polymer as compared to the reference cement paste. Nevertheless, a numerous studies stated that the presence of T-PEG polymer in the cementitious mixture inhibited the nucleation and growth of calcium-silicate hydrates (C-S-H) [18, 36, 45] while the morphology of hydration products can be altered [35, 46–48].

At the same time, there is more COO^- ions can be dissociated in the alkaline cement solution when the amount of AA in the particular T-PEG polymer increased. Then, more COO^- ions was attracted to the Ca^{2+} ions which formed on the surface of cement particles, in order to accelerate the dispersion of cement paste particles to improve the fluidity of the cement paste. In addition, there were more formation of hydrogen bonds between oxygen atoms of ether bonds and water molecules, which enhanced surface tension and increased intermolecular interaction [10, 37]. Thereby, a continuous reduction trend can be seen on the water demand for the cement paste with T1, T1.5 and T2 due to the increment AA content.

This particular trend was not been followed by the cement paste with T2.5 and T3.5 respectively, in which water-cement ratio was higher than cement paste with T2. For this, the concentration of ionic functional group in this particular T-PEG polymer was too high and a large physical barrier was created within the calcium chelate complexes [18, 49, 50]. Furthermore, the reduced PCE side chain density limits steric hindrance effect, which reduced cement particles distribution [8, 36]. Thereby, the water demand was increased again to reach required standard consistency level.

Flow Retention Test

The flow retention test was investigated to determine the dispersion maintaining ability of the polymer. The concept of a high flow diameter stood for a strong dispersing capacity [19]. Table 7 tabulates the change in flow diameter of fresh paste at 0.5 hour intervals after mixing for 2 hours. It was found that the flow diameter of the fresh paste was decreased with the time, indicating the dispersion-retaining capacity of cement paste with all T-PEG polymer decreased with time [51].

Table 7. The change in flow diameter of fresh paste.

Mix Design	Flow diameter (mm)					Water-Cement Ratio
	Initial	0.5 hour	1.0 hour	1.5 hour	2.0 hour	
Reference	195	150	130	110	100	0.53
T1	200	145	105	100	100	0.46
T1.5	185	150	120	100	100	0.49
T2	200	145	110	100	100	0.43
T2.5	185	145	110	100	100	0.43
T3.5	195	175	120	100	100	0.48

Besides, it was also observed that the mortars with an addition polymer of T1, T1.5, T2, and T2.5 had similar flow diameters within these two hours as compared to the reference mortar. While, the mortar with polymer T3.5 provides better flow retaining ability than remaining polymer. It retained a higher flow diameter, which is 175 mm in the first 0.5 hours as compared to the others. In the next subsequent 0.5 hour, the mortar flow for mortar with polymer T3.5 decreased to 120 mm and 100 mm, respectively.

For reference mortar, a high water demand was needed during mixing process to reach estimated mortar flow, creating high solid-liquid interfacial energy in the cement-water system [37]. It entrapped a number of available free water within binder particles cluster in fresh mortar and help to disperse cement particles with good retention ability [5, 18, 38].

By referring to mortar with T-PEG polymers, these mixtures have similar flow diameter change as reference mortar, even though low water amount used during mixing process. The presence of T-PEG polymer in the cement-water system used to lower surface tension of cement-water system while modifying solid-liquid interfacial energy [37, 52]. At the same time, it released COO^- to have interaction with Ca^{2+} from cement particles, producing a plenty of calcium chelate complexes. In other words, it formed an obstacle to the diffusion of water and Ca^{2+} across the water-cement interface [5, 35, 40]. Thus, it enhanced initial dispersion ability and dispersing maintaining ability.

As well, polymer T3.5 released high amount of COO^- ions during cement hydration and possessed higher electrostatically adsorption on the polar surface of cement particles [11]. At the same time, the adsorption layer can be more compact as compared to the remained mortar mix. There were more adsorption sites on the molecules which helped in the dispersing action [5, 18, 53]. This indicates that at the same dosage, the increasing of the carboxylate group in the polymer improved the adsorption amount of PCEs on the cement particles. Furthermore, authors have reported that the higher content of the carboxylic group in the polymer possesses a higher molecular weight to produce excellent dispersion abilities [18, 54]. In addition, low side chain density of polymer T3.5 is beneficial to initial dispersion ability and dispersion maintaining ability also. It managed to release free water molecule in cement-water system to decrease the thickness of water film formed on the surfaces of cement particles [37]. Consequently, the polymers should consist of a short trunk polymer but a long graft chain with low side chain density to achieve high dispersibility [55].

Flexural Strength

Table 8 showed the results of average mortar flexural strength at various ages and it was normalized with the average strength of reference mortar at the same time. It was observed that each of the mortar mix possessed an upward trend in mortar flexural strength from curing ages of 7 days to 28 days, with an exception of mortar with polymer T1. The mortar with polymer T1 exhibited 6.1 MPa mortar flexural strength at early 7th days but reduced to 5.9 MPa at 28th curing days. It is probable that an uneven distribution of absorbed polymer molecules formed a mosaic structure with cement particles during cement hydration process [6, 47]. Hence, the side chain of T1 polymer induced steric hindrance effect that dispersed paste particles unevenly and greatly reduced the formation of localized agglomeration [42, 56].

Table 8. The average flexural strength and normalized flexural strength to the reference mortar.

Mix Design	Average Flexural Strength and Normalized Flexural Strength to Reference Mortar				Water-Cement Ratio
	Day-7		Day-28		
	(MPa)	(%)	(MPa)	(%)	
Reference	5.0	100	6.3	100	0.53
T1	6.1	122	5.9	94	0.46
T1.5	4.9	98	5.9	94	0.49
T2	6.3	126	6.3	100	0.43
T2.5	6.0	120	6.2	98	0.43
T3.5	5.3	106	6.1	97	0.48

Based on the result obtained, reference mortar achieved flexural strength of 5.0 MPa in early 7 days and increased to 6.3 MPa at 28 days. It can be seen that a significant improvement in the early flexural strength with the presence of T-PEG polymer, with an exception of mortar with polymer T1.5. The mortar flexural strength was increased to 6.3 MPa in

early 7 days with the polymer T2 in the mortar mixture. In spite of the fact that low water amount in the mortar with T-PEG polymer, T-PEG polymer also contribute COO^- into the cement-water system to interact with Ca^{2+} from cement particles during early cement hydration. It produced a strong chelation effect through an effective amount of the macromolecule adsorbed to an individual cement grain, which formed a number of calcium chelate complexes within binder particles [5, 13]. Hence, an improvement on mortar flexural strength can be provided through the modification of the mortar microstructure.

However, mortar with polymer T2.5 and T3.5 exhibited lower mortar flexural strength than mortar with polymer T2, at curing ages of 7 days and 28 days. As compared to polymer T2, these two polymers theoretically contributed more COO^- for electrostatically absorption onto cement grains, with its higher AA amount during synthesis process. This resulted in the agglomeration of cement particles when the main chain of the polymers absorbed on several cement particles, which hindered cement hydration [5]. At the same time, low PEO side chains in these two polymers leads to a decrease of the steric hindrance effect, which caused an agglomeration effect on the binder particles [5, 36]. Thus, it caused a poor distribution of binder particles and aggregates during cement hydration process, which in turns resulted in lower mortar flexural strength produced [5, 35, 57].

Compressive Strength

Table 9 showed the results of average mortar compressive strength at various ages while the normalization of the average strength to the reference mortar was determined. Likewise, an increasing trend of mortar compressive strength was attributed by each of the mortar mixtures within these 28 days, as same as mortar flexural strength. It can be mainly attributed to the refinement in the mortar microstructure which caused by continuous hydration process along curing durations [58].

Table 9. The average compressive strength and normalized compressive strength to the reference mortar.

	Average Compressive Strength and Normalized Compressive Strength to Reference Mortar				Water-Cement Ratio
	Day-7		Day-28		
	(MPa)	(%)	(MPa)	(%)	
Reference	30.8	100	37.1	100	0.53
T1	39.3	128	43.5	117	0.46
T1.5	32.1	104	32.6	88	0.49
T2	40.7	132	41.7	112	0.43
T2.5	36.0	117	42.3	114	0.43
T3.5	31.6	103	34.0	80	0.48

At 7 days of curing ages, it can be seen that mortar with any T-PEG polymer exhibited higher mortar compressive strength than reference mortar, with an increment of 4 % to 32 %. For example, mortar with polymer T2 exhibited an increment up to 32 % on the mortar compressive strength, as compared to reference mortar. It was mainly attributed to low water-cement ratio used to achieve estimated flow level in fresh state, while providing a refinement in the pore structure to improve mortar microstructure [59].

With reference to the 28 days mortar compressive strength results, mortar with polymer T1.5 and T3.5 exhibited lower strength than reference mortar. Both of them only retained 88 % and 80 % of mortar compressive strength when compared to reference mortar, respectively. As mentioned, it was probable that formation of mosaic structure occurred in these mortar mixture during cement hydration process [6, 47]. Thus, it was advisable to access the performance of these T-PEG polymers in cementitious composites by keep investigating long-term mortar compressive strength, which prolonging curing durations up to 180 days.

CONCLUSIONS

From the investigation and result analysis, the following conclusions are summarized:

- The fluidity of the cement paste can be improved with an optimum grafting density of the main chain and side chain.
- The cement paste with T2 polymer required the lowest water to reach standard consistency level due to optimum condition of electrostatic repulsion force and steric hindrance effect.
- The mortar with T2 polymer exhibited the best performance on both flexural and compressive strength tests.
- The increasing main to side chain densities ratio of T-PEG polymer imposes a significant influence on the fresh and hardened properties of the concrete material produced.
- For the future work, it is recommended to evaluate durability performance of these T-PEG polymers in mortar and/or concrete applications, in terms of water absorption, intrinsic air permeability, total porosity, drying shrinkage, carbonation resistance and chloride diffusivity for a comprehensive body of knowledge on the performance of the concrete material containing T-PEG polymers.

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