Effect of some polymers and asphalt emulsion on the deterioration of cement mortar and concrete

I.M. Ibrahim, N.F. Ghaly, M. El-Shafie and A.M.M. Abd El Rahman

Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt
dr_ismailmohamed@yahoo.com

Abstract: Deterioration of concrete due to chemical attack is a serious menace to the two major properties of concrete; strength and durability. This paper reports experimental findings regarding the performance of anionic slow set asphalt emulsion with latex and acrylic emulsions modified concrete. Laboratory tests were conducted to measure the main properties such as air content, compressive strength, and flexural strength, modulus of elasticity, water absorption and drying shrinkage. Results have shown that inclusion of appropriate quantities of asphalt emulsion to latex and / or acrylic emulsions into concrete plays a significant role in air content, water absorption and drying shrinkage. From the scanning electron microscope (SEM) analysis showed that the cement paste samples with introducing asphalt emulsion to latex and / or acrylic emulsions have greater numbers of air voids but with ultimately smaller total voids content compared to control mix.

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Key words: Cement concrete, compressive strength, water absorption

1. Introduction

Polymer concrete has been widely used for repair and overlay of deteriorated concrete pavements, airport runways, and bridge decks as well as fabrication of precast products due to its well-known advantages in hardening time, freezing and thawing resistance, corrosion resistance, compressive strength, splitting tensile strength, flexural strength, and bond strength [1]. Polymer-modified cements which prepared by mixed cement and polymer emulsion together have been widely used for structures attribute to their increased bond strength, reduced permeability [2].In modern concrete construction and repair works the role of polymers is increasing day by day. Polymers are either incorporated in a cement–aggregate mix or used as a single binder. The composites made by using polymer along with cement and aggregates are called polymer-modified mortars (PMM) or polymer-modified concrete (PMC), while composites made with polymer and aggregates are called polymer mortar (PM) or polymer concrete (PC) [3].

Adding aqueous polymer emulsions or re-dispersible polymer powders in the fresh concrete mix make polymer modification of concrete. The polymer emulsion is stabilized by surfactants, and each polymer has its own film forming properties within the applicable temperature range and the physicochemical conditions during hardening and curing. The surfactants and the low film forming ability of most emulsions are generally hindering the building of high performing and durable microstructures in the PCC. The process allows building up of composite polymer cement microstructures on a nano-scale, which can avoid the negative influences of the polymer admixtures cement interactions on the shape and distribution of the cement hydrate crystals, and on the transition zones between cementitious binder matrix and aggregates [4].There have been several research studies on the polymer concrete using latex emulsions [5,6]. Polymer latexes are known to affect the physical, mechanical and durability properties of Portland cement paste, mortar and concrete. The magnitude of this effect is dependent on the type of latex and the latex concentration in the mixture [7, 8]. Latexes have been employed to dramatically increase on the tensile and flexural strength [9]. Latexes have the superiority of the other ordinary admixtures by its double effect on the modifying of the characteristics of concrete. Similarly with the ordinary admixtures, the first effect is the high reducing on concrete water content due to the presence of a high range superplasticizer agent on latex constituents [10]. Also, there has been several research studies on the polymer concrete using an MMA–polymethyl methacrylate (PMMA) system as a binder [11-14], but most of them focused on the polymer concrete employing tri methyl opropane tri meth acrylate (TMPTMA) as a cross-linking agent. Very few research efforts have been made on the MMA–PMMA polymer concrete using MAA, one of the polar monomers serves as an auxiliary accelerator.

2. Material and Experimental Procedures

2.1. Materials and material mix-proportions

Anionic asphalt emulsion, acrylic emulsion and natural rubber latex treated with10% polyvinyl acetate was used. The physical properties of asphalt emulsion are shown in Table 1. Chemical analysis of latex and acrylic emulsions are presented in Table 2 and Table 3, respectively. Ordinary Portland cement complying with Egyptian Standard Specification E.S.S 373/1993 was used. Fine aggregate and crushed limestone as coarse aggregate complying with Egyptian Standard Specification E.S.S 1109/1971 was used. Properties and gradation of the aggregates used are summarized in Table 4, and Table 5. Cement content and w/c ratio are 350 kg/m3 and 0.5 respectively. Superplasticizer high rang water-reducing chemical admixture Sikament 163 produced by the Sika Egypt Company was used. It complies with ASTM C 494 type F and B.S. 5057 part 3 for Superplasticizer.

2.2. Methods of Preparation:

Four different types of polymer namely, acrylic emulsions P1, latex emulsion P2, acrylic emulsions with anionic asphalt emulsion (1:1) P3 and latex emulsions with anionic asphalt emulsion (1:1) P4were selected beside the control mix.

2.2.1. Preparation of anionic asphalt emulsion (50% active material):

Emulsions are manufactured by passing hot asphalt and water containing emulsifying agents through a colloid mill under high pressure. The colloid mill produces extremely small (less than 5-10 μ) globules of asphalt, which are suspended in water. Table 2 presents the main properties of anionic asphalt emulsion.

2.2.2. Preparation of modified anionic asphalt emulsion P3 and P4:

The anionic asphalt emulsion just after the emulsification of asphalt was added to the emulsified polymers acrylic and /or latex to produce P3 and P4, respectively. Taking into consideration that, the asphalt polymer ratio was 1:1 by weight, stirring was completed, i.e. until the emulsion became completely homogeneous.

2.2.3. Preparation of mortar sample:

Cement: sand: water ratio of 1:2:0.5 was used. The control mix was prepared by dry mixing of cement and sand until homogenous distribution of the materials. Total water content was then added to the dry mix with continued together for 2 min. The amount of water in the polymer solution was included in the water-to-cement ratio. To make the polymer-modified mortar cement, sand and water were first mixed for 2 min and then the polymer solution was mixed with the pre-wetted mortar for 5 min at 125 rpm.

2.2.4. Preparation of concrete sample:

The control mix was prepared by dry mixing of cement (350 kg/m^3), sand (665 kg/m^3), aggregate $size_1$ (470 kg/m^3) and aggregate $size_2$ (705 kg/m^3), until homogenous distribution of the materials. Total water content (180 lit/m^3) was then added to the dry mix with continued together for 2 min at a speed of around 350 rpm and then for another 1 min at a speed of around 250 rpm.

To make the polymer-modified concrete, cement, sand, gravel, and water were first mixed for 2 min at 350 rpm, and then, the amounts of polymer added were again 4%, 6%, 8% and 10%, based on the weight of cement. The amounts of water in the polymer solution were included in the water-to-cement ratios. The polymer solution was mixed with the pre-wetted concrete for 1 min at 250 rpm, superplasticizer was added to the fresh concrete during mixing to achieve a uniform mix with about 180 mm slump.

2.3. Testing methods

2.3.1. Fresh and hardened mix properties of concrete was conducted based on using an Air content, Compressive strength, Flexural strength, Modulus of elasticity, Water absorption were carried out according to ASTM C231, BS 1881, ASTM C293**,** ASTM C469,and ASTM C127, respectively**.** Compressive strength was measured at 28, 90 and 180 curing days at 23 $^{\pm 2}$ ºC and 98 $^{\pm 1}$ % of relative humidity. Flexural strength, modulus of elasticity and water absorption was measured at 28 days.

2.3.2. Shrinkage measurement:

The shrinkage measurements were carried out from 1 day to 210 days on the hardened mortar mix samples cured in a cabinet at 65% relative humidity at 23 ± 2 ºC [4]. Specimen dimension was 25×25×285 mm for shrinkage.

2.3.3. Scanning electron microscope SEM analysis was carried out on both modified and unmodified asphalt emulsion samples. All the samples were gold coated to prevent charging effects.

Table 1: Physical properties of anionic asphalt emulsion

Physical properties	Value
Test on emulsion:	
- Viscosity – Saybolt Furol at 25°C.	26
- Settlement and storage stability test 24h %.	0.6
- Sieve test %.	0.1
- Residue by Evaporation of Emulsified Asphalt at 163 °C. %	63.4
- Residue from distillation to 360 °C, %	62
- Drying time, min.	28
- Solubility in water.	good
Test on residue from distillation:	
- Penetration at 25°C 100 g, 5 seconds, 0.1 mm	42
- Ductility at 25 °C, 5 cm/min, cm.	+100
- Solubility in trichloroethylene, %.	98

Table 2: Physical properties of latex emulsion

Property	Value
Total solid content (%)	61
Dry rubber content (%)	60
Non rubber contents (%)	1.5
pH	10
Mechanical stability time (s)	1227

Figure 1: Preparation of dry shrinkage specimens

Table 3: Physical properties of acrylic emulsion

Physical properties	Value
Solid content (%)	50
pH	9
Viscosity 30 °C by Brookfield RVT, Sp. 320 rpm (poise).	
Particle size of solid material (μ)	8
	0.58

Table 4: Aggregate properties

Properties	Value
- Coarse aggregate (ASTM C 127)	
Bulk specific gravity, g/cm^3	2.698
Apparent specific gravity, g/cm^3	2.714
Absorption, %	1.73
- Fine aggregate (ASTM C 128)	
Bulk specific gravity, g/cm^3	2.683
Apparent specific gravity, g/cm^3	2.735
Absorption, %	1.92

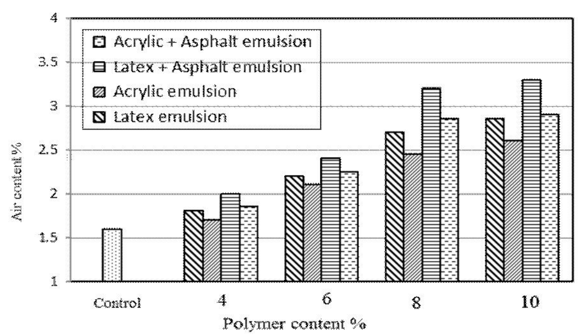

Figure 2: Effect of polymer types and polymer content on air content

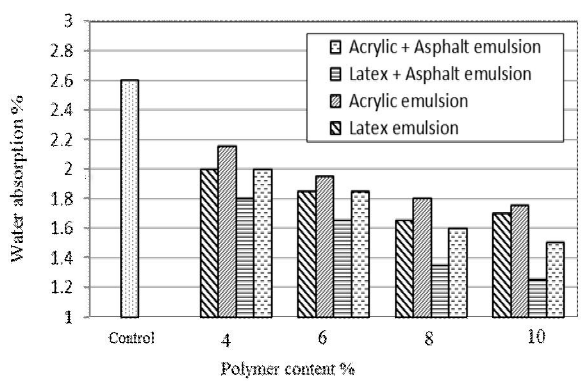

Figure 3: Effect of polymer types and polymer content on water absorption

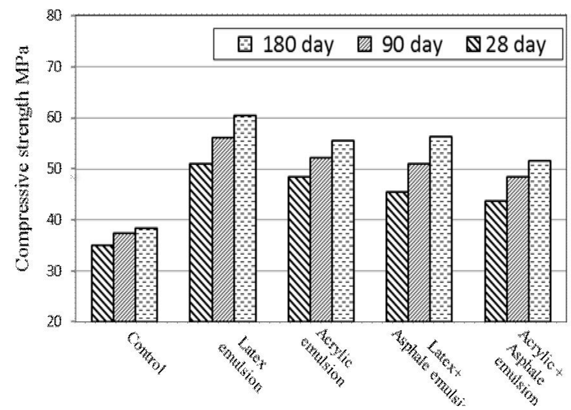

Figure 4: Effect of polymer types on compressive strength

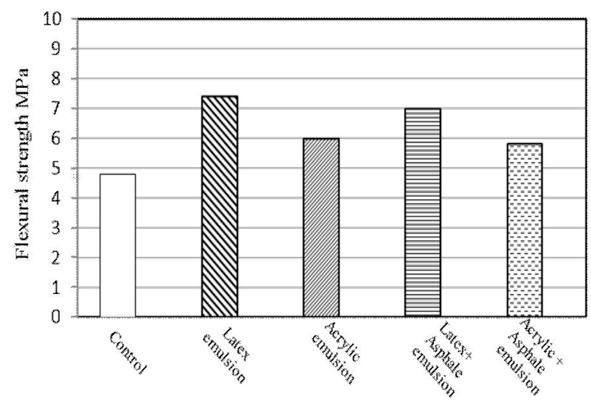

Figure 5: Effect of polymer types on flexural strength

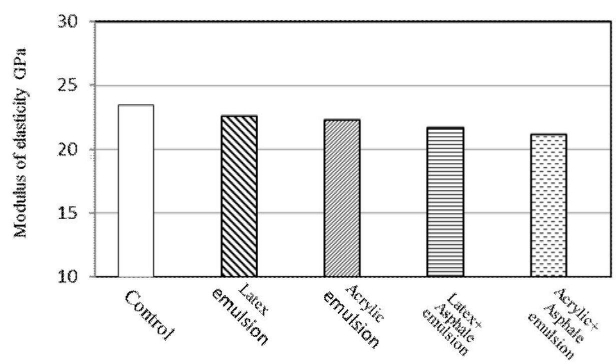

Figure 6: Effect of polymer types on modulus of elasticity

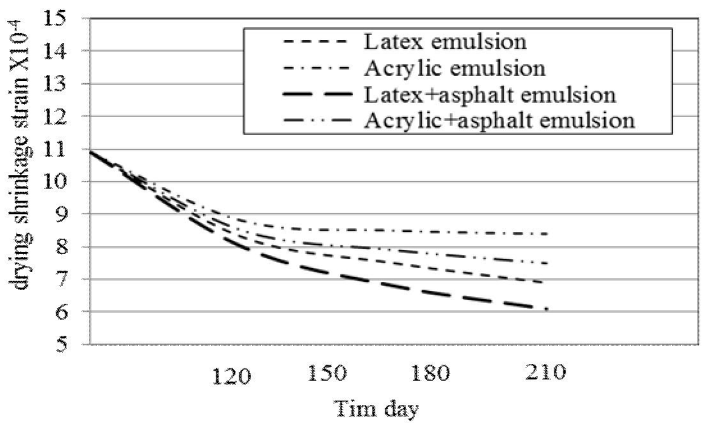

Figure 7: Effect of polymer types on drying shrinkage strain

Table 5: Gradation of the aggregates used

Screen size (mm)	Properties					
	Coarse aggregate size 2		Coarse aggregate size 1		Fine aggregate	
	Pass %	Limit %	Pass %	Limit %	Pass %	Limit %
25	100	100	-	-	-	-
19	92.5	85-100	100	100	-	-
12.5	31.3	0-70	100	90-100	-	-
9.5	3.74	0-25	89.6	85-100	-	-
4.75	0.7	0-5	8.3	0-10	100	95-100
2.36	-	-	1.1	-	97	80-100
1.18	-	-	-	-	97.5	50-85
0.6	-	-	-	-	48	25-60
0.3	-	-	-	-	27.1	10-30
0.15	-	-	-	-	2.7	0-10

Table 6: Effect of polymer types and polymer content on physical properties of concrete mix

Mix No.	Air content %	Water absorption %	Compressive strength MPa			Flexural strength MPa	Modulus of elasticity GPa
			28 Day	90 days	180 days		
Control	1.60	2.60	35.0	37.5	38.6	4.8	23.5
Mix 1	1.80	2.00	39.8	42.4	46.0	-	-
Mix 2	2.20	1.85	43.6	47.0	50.3	-	-
Mix 3	2.70	1.65	51.0	56.2	60.4	7.4	22.6
Mix 4	2.85	1.70	52.2	56.9	61.7	-	-
Mix 5	1.70	2.15	36.5	38.6	40.6	-	-
Mix 6	2.10	1.95	40.2	42.8	45.0	-	-
Mix 7	2.45	1.80	48.5	52.2	55.5	6.0	22.3
Mix 8	2.60	1.75	49.8	53.0	56.7	-	-
Mix 9	2.00	1.80	33.7	36.5	40.9	-	-
Mix 10	2.40	1.65	47.1	40.4	45.7	-	-
Mix 11	3.20	1.35	45.5	51.0	56.3	7.0	21.7
Mix 12	3.30	1.25	46.6	51.3	57.4	-	-
Mix 13	1.85	2.00	32.0	35.1	36.0	-	-
Mix 14	2.25	1.85	36.1	39.6	42.2	-	-
Mix 15	2.85	1.60	43.8	48.5	51.7	5.8	21.2
Mix 16	2.90	1.50	45.0	50.2	53.3	-	-

M_1-M_4 Containing latex emulsion M_5-M_8Containing acrylic emulsion M_9-M_{12} Containing latex with asphalt emulsion
M_{13}-M_{16} Containing acrylic with asphalt emulsion

Photo 1: unmodified cement paste

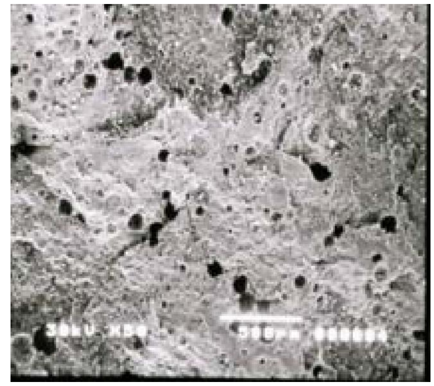

Photo 2: Cement paste with latex emulsion

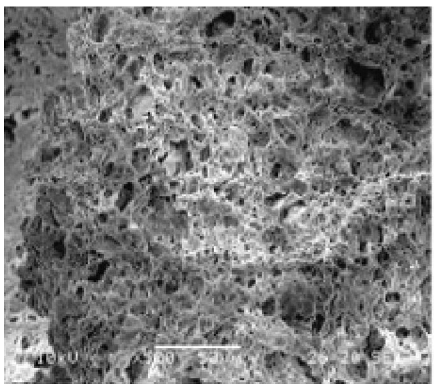

Photo 3: Cement paste with acrylic emulsions

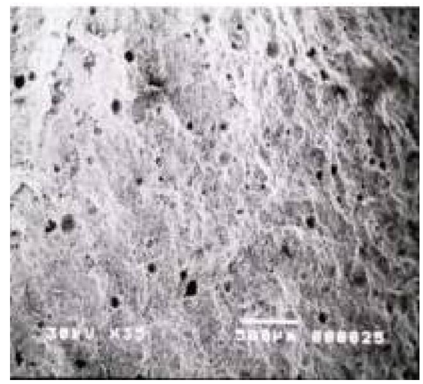

Photo 4: Cement paste with latex and asphalt emulsions

Photo 5: Cement paste with acrylic and asphalt emulsions

Photos 1-5: Scanning electron microscope analysis of hardened modified and unmodified cement paste

3. Results and Discussion

3.1. Air content

The air content was measured after completion of mixing. The result of the change in air contents in the fresh polymer-modified concrete mix is given in Table 6 and Figure 2. The air content of the modified concrete mix is higher than the unmodified mix. The highest increase in air contents was obtained with 10% modifier contents, whereas no significant difference in air content entrained between 8% and 10% polymer content. The percentage of increase in air content at 8% polymer content was 69%, 53%, 100% and 78% for latex emulsion, acrylic emulsion, asphalt emulsion with latex and asphalt emulsion with acrylic, respectively, compared with the control mix. Inclusion of asphalt emulsion into polymer emulsion has increased in the air content percent. Because of the surfactants used in the manufacture of emulsions, excessive amounts of air can be entrained when modifiers are mixed into a Portland-cement system.

3.2. Water absorption

The effects of polymer and asphalt emulsion addition on the permeability characteristics of cement mortars are presented in Table 6 and Figure 3. According to the figures, the permeability of polymer modified was found to be lower than that of the unmodified controls. While, the permeability of polymer with asphalt emulsion was found to be much lower than that of the modified and unmodified specimen. Low permeability properties of the samples containing asphalt emulsion were attributed to the fact that asphalt particles, being much smaller than the sand and cement particles, filled the smaller voids and eventually coalesced into a monolithic film that surrounded the aggregate and coated the cement. The reduction in water absorption at 8% polymer content was 36%, 31%, 48% and 38% for latex emulsion, acrylic emulsion, asphalt emulsion with latex and asphalt emulsion with acrylic, respectively, compared with the control mix. This behavior may be attributed to a pore sealing phenomenon, polymer coalesces in the pores of paste, after the withdrawal of water by hydration of cement, sealed these pores preventing past to absorb high amounts of water.

3.3. Compressive strength:

The results of polymer addition on compressive strength of the concrete mix at 28, 90 and 180 days are shown in Table 6 and Figure 4.Compressive strength of unmodified concrete mix specimen is 35 MPa, 37.5 MPa and 38.5 MP at 28, 90 and 180 day, respectively. For both polymer systems the compressive strength is better than that of the control specimens at 10% polymer–cement ratio, whereas no significant difference in compressive strength between 8% and 10% polymer content. The highest strength gain was achieved by the use of latex emulsion, closely followed by acrylic emulsion. On the other hand, lowest compressive strength value was observed against acrylic with asphalt emulsion. Differences in the types of the compositional substances present in the polymers are believed to be responsible for the variations in the compressive strength. When latex/cement ratio was8% the compressive strength was 51 MPa, 56.2 MPa and 60.4 MPa at 28, 90 and 180 day respectively, while that of acrylic/cement ratio was 8% the compressive strength was 48.5 MPa, 52.2 MPa and 55.5 MPa at 28, 90 and 180 day respectively, Inclusion of asphalt emulsion into polymer emulsion has increase in compressive strength compared with the unmodified sample, while it has reduction in compressive strength compared with the polymer latex and /or acrylic mix alone. Comparing the results in 28 day and 180 day, it can be also seen that air cured polymer modified samples demonstrated better performance than water cured ones with a sole exception of the unmodified sample. It is assumed that water curing would reduce the effectiveness of polymers in the modified specimens, because polymer latex films could not be formed under water curing.

3.4. Flexural strength:

The effect of polymer–cement ratio on 28 days flexural strength of different compositions is shown in Figure 5. It can be seen that the flexural strength of the unmodified water cured mortar is 4.8 MPa, However, for both polymer systems the flexural strength is better than that of the water cured control specimens at 10% polymer cement ratio, whereas no significant difference in flexural strength between 8% and 10% polymer content. The increase in flexural strength of latex emulsion is up to 54% as compared to unmodified sample while it is about 23% for the acrylic emulsion sample at 8% polymer–cement ratio. This shows that latex emulsion should behave better than acrylic emulsion under flexural loading. Inclusion of asphalt emulsion into polymer emulsion has increase in flexural strength compared with the unmodified sample, while it has a reduction of flexural strength compared with the polymer (latex or acrylic) mix alone.

3.5. Modulus of elasticity:

The effect of different types of polymer on modulus of elasticity is shown in Figure 6. It can be seen that the modulus of elasticity of the unmodified water cured samples after 28 days is 23.5 GPA, However, for both polymer systems the modulus of elasticity is better than that of the control specimen at 10% polymer–cement ratio, whereas no significant difference in modulus of elasticity between 8% and 10% polymer content. The modulus of elasticity at 8% polymer content is about 4%, 5%, 8% and 10% for latex emulsion, acrylic emulsion, latex with asphalt emulsion, and acrylic with asphalt emulsion, respectively compared to unmodified sample. Inclusion of asphalt emulsion has improved in modulus of elasticity compared with the modified and unmodified samples.

3.6. Drying shrinkage:

Results of drying shrinkage or length change of mortar samples are presented in Figure7. The figure shows that modified polymer emulsion mortar shrank less than unmodified mortar did at all ages. When the shrinkage value at five months was considered, the shrinkage of modified polymer emulsion mortar samples showed considerable reduction compared with unmodified mortar shrinkage. Compared with unmodified mortar, the shrinkages of mortar containing 8% latex emulsion, acrylic emulsion was 23% and 31%, respectively, at the end of five months. While, the shrinkages of mortar containing 8% latex with asphalt emulsion and acrylic with asphalt emulsion was 37%, and 44% respectively, at the end of five months.

Based on the strength and shrinkage measurement results, it can be concluded that the latex with asphalt emulsion could be utilized in cement-based materials as a mineral additive particularly in concrete pavement, large industrial concrete floors, parking lot applications or rock bolt applications of rock engineering where shrinkage should be avoided.

3.7. Porosity and pore size distribution

SEM images were used to characterize all the samples and allowed to identify their microstructure. Large air voids, with a diameter of about 40–60µm, were found in the unmodified sample, as shown in photo 1, while, small cavities were observed in the samples containing latex and acrylic emulsions, as shown in photo 2 and 3, Furthermore it was interesting to observe that the inclusion of asphalt emulsion into polymer has air voids size smaller than both the modified and unmodified samples as shown in photo 4 and 5.

4. Conclusions

This study focused on investigating the effect of polymer emulsions (latex, acrylic and asphalt) on the mechanical properties of cement and concrete based on a series of laboratory experiments. The results of this study point to the following conclusions at 8% polymer–cement ratio:

- Inclusion of asphalt emulsion into polymer emulsion significantly effect of air content number but the decrease of the air voids volume and improves air voids distribution.
- The water absorption reduces when the polymer modified was added. However, at the same amount of polymer- cement ratio polymer with asphalt emulsion showed slightly better properties than polymer emulsion alone.
- Inclusion of asphalt emulsion into polymer emulsion improves of drying shrinkage about 61% and 42% than latex emulsion and acrylic emulsion, respectively.
- The addition of polymer to concrete mix improves the compressive strength about 60% and 47% for latex emulsion and acrylic emulsion at 180 days, respectively compared to unmodified sample.
- Increase in flexural strength of latex emulsion is up to 54% while it is about 25% of the acrylic emulsion sample. Inclusion of asphalt emulsion into polymer emulsion has increased in flexural strength compared with the unmodified sample, while it has a reduction in flexural strength compared with the polymer emulsions alone.
- All polymer systems gave better modulus elasticity than that of the control specimen at 8% polymer–cement ratio. The modulus of elasticity was about 4%, 5%, 8% and 10% for latex emulsion, acrylic emulsion, latex with asphalt emulsion, and acrylic with asphalt emulsion, respectively compared to unmodified sample. Inclusion of asphalt emulsion has improved in modulus of elasticity compared with the modified and unmodified samples.
- The large air voids diameter was found in the unmodified sample, while, small cavities were observed in the samples containing latex and acrylic emulsions, Furthermore it was interesting to observe that the inclusion of asphalt emulsion into polymer has air voids size smaller than both the modified and unmodified samples.

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