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Rationalizing the Recycling of Polymers from the Paint Industry During Production of Sustainable Concrete

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Abstract: The amount of leftover paint generated by households is estimated to be among the largest volume of liquid wastes collected by municipalities and state agencies, thus making its disposal a major concern for environmental and economical reasons. At the same time, the concrete industry is gradually shifting towards green materials and recycling programs with special focus on sustainable development. In this context, this paper is part of a comprehensive research project undertaken to evaluate feasibility of recycling waste latex paints (WLPs) during concrete production. Tested WLPs were not randomly collected from waste collection sites, rather produced to ensure traceability of composition, then stored in sealed or opened pail conditions to expire. Test results have shown that workability, air content, and setting time of freshly mixed concrete are directly affected by WLP constituents, substitution rate, and storing conditions. The concrete splitting tensile strength and bond to embedded steel bars showed considerable improvements with WLP additions.

Keywords: Concrete, Waste Latex Paint, Recycling Polymer, Workability, Compression, Tensile, Bond to Steel

1. Introduction

The use of industrial wastes such as scrap rubber, glass, plastic bottle fibers, and used engine oil as raw materials for the concrete construction industry has considerably increased over the last years (Earth-Tec Canada, 2001). Waste latex paints (WLPs) are among the toxic wastes whose proper management raises major environmental and economical concerns to municipalities and state agencies. Their improper disposal could contaminate water, harm fish and wildlife, and cause sewage systems to be less effective.

WLPs have several engineering characteristics that could enhance sustainability of concrete materials. For instance, Mohammed et al. (2008) evaluated the effect of substituting mixing water by 5% to 25% WLP on fresh and hardened properties of concrete containing 280 kg/m^3 cement and 0.4 water-to-cement ratio (w/c). Tested WLP had 45% solid content and viscosity of 90 mPa.s. The authors observed gradual improvement in slump and compressive strength up to around 10% WLP, while higher substitution rates led to reduction in both workability and strength. The addition of WLP led to increased flexural strength at all substitution rates, which was attributed to the high tensile strength of latex films and bond improvement at the hydrated paste-aggregate interfacial transition zone (Mohammed et al., 2008). Similar conclusions were drawn by Nehdi and Sumner (2003) when testing WLP having 30% solid content composed of 15% polymers, 12.5% titanium dioxide pigment, and 12.5% extenders. The drop in compressive strength at relatively high WLP rates was attributed to a set-retarding effect along with increased air content. Durability tests including freeze-thaw, chloride penetrability, surface scaling, and leaching of toxic metals showed all positive preliminary results.

Various aspects require further investigations to widespread and formalize the use of WLPs in concrete. For example, lack of information exists in literature regarding the transfer of forces and bond stress-slip behavior of WLP-modified concrete with embedded steel bars. Also, the effect of WLP constituents and storing conditions on concrete fresh and mechanical properties is not yet understood. In fact, such wastes are made of different latex types and contents as well as pigment/extender ratios that lead to synergetic effects on cement aptitude to flow and hydration processes. In other words, it is not clear whether the results published in literature would still be valid if WLPs containing different types of polymeric latexes and/or possessing different viscosity levels or solid contents were collected and used for concrete production. This fact was admitted by various researchers (Nehdi and Sumner, 2003; Mohammed et al., 2008; Almesfer et al., 2012) who recommended additional investigations to evaluate variability of WLPs on concrete behavior.

The predominant types of binders used in latex-based paints include acrylic copolymers such as vinyl acetate (VA) and pure acrylate (PA) (Lambourne and Strivens, 1999). These latexes consist of very small polymer particles (0.05–5 μm) formed by emulsion polymerization and stabilized in water with the aid of anionic and/or nonionic surfactants. The selection of given binder type is mostly related to the desired paint gloss and film properties such as scrub resistance, adhesion, and water absorption. From the other hand, powders in paints can broadly be divided into two categories including pigments (0.1–1 μm) and extenders (0.5–15 μm) (Chern, 2008). The titanium dioxide (TiO_2) is the pigment that provides whiteness and constitutes the main source of hiding (or, opacity) for paints. Its concentration typically varies from as low as 2.5% for colored pigmented paints up to 15% for white paints. Extenders such as calcium carbonate ($CaCO_3$), clay, silica, talc, and chalk are incorporated to ensure the bulk material at relatively low cost (Chern, 2008).

Recently, Assaad (2015 and 2016) adopted a rational approach to evaluate the effect of WLP constituents on flow and rheological properties of cement pastes along with their compatibility with high-range water reducers (HRWRs). The WLPs were not randomly collected from waste collection sites, rather produced and stored under different conditions to expire. The paint formulations contained different VA and PA-based latex concentrations; the TiO_2 varied from 2.5% to 15%, while $CaCO_3$ adjusted to secure similar solid contents. The author found that flowability of modified cement pastes improved at polymer/cement ratio (p/c) lower than around 0.25%; but then dropped at higher p/c due to the relative increase in mixture stickiness. A series of charts based on the gloss unit of paints and their pigment-volume-concentrations were proposed for predicting variations in flow, yield stress, and plastic viscosity following WLP additions in cementitious materials (Assaad, 2015 and 2016).

This paper is the continuation of a research project undertaken to evaluate feasibility of recycling waste latex paints (WLPs) during concrete production. Its main objective is to validate the data obtained using cement pastes through the evaluation of WLP constituents, substitution rate, and storing conditions on concrete properties. The substitution rates of mixing water by WLPs were 5% and 10%. Data reported herein can be of particular interest to concrete producers, municipalities, and environmental organizations to economically and efficiently manage the recycling of WLPs.

2. Experimental Program

2.1. Production of WLPs Used in This Project

2.1.1. Constituents and Proportions of Latex-based Paints

Table 1. *Constituents of VA and PA-based paints produced and properties of corresponding WLPs.*

	Paint no. 1		Paint no. 2		Paint no. 3		Paint no. 4		Paint no. 5	
Water, %	45.16		39.27		39.84		41.34		35.43	
VA latex, %	15		25		25		0		0	
PA latex, %	0		0		0		25		35	
TiO_2, %	15		15		2.5		15		15	
$CaCO_3$, %	22		18		30		16		12	
$TiO_2/CaCO_3$ ratio	0.68		0.83		0.08		0.94		1.25	
Additives*, %	2.84		2.73		2.66		2.66		2.57	
	Paint properties determined after production									
Solid content, %	44.93		45.87		45.37		44.13		45.02	
pH	9.3		9.2		9		9.1		9.2	
Density, g/cm^3	1.24		1.23		1.25		1.18		1.2	
Viscosity, Pa.s	0.105		0.106		0.12		0.11		0.115	
Scrubbing, cycles	2940		4010		4260		6100		6730	
Gloss unit	9		15		6		67		75	
Opacity, %	89		93		67		88		93	
	WLP properties after 6 months storage in sealed (S) or opened (O) pail conditions									
WLP codification	15VA -0.68 -S	15VA -0.68 -O	25VA -0.83 -S	25VA -0.83 -O	25VA -0.08 -S	25VA -0.08 -O	25PA -0.94 -S	25PA -0.94 -O	35PA -1.25 -S	35PA -1.25 -O
Solid content, %	45.5	53.6	45.5	49.4	46.1	58.2	45.6	54.6	46.2	56.8
pH	8.1	7.9	8.4	8	7.7	7.4	7.9	8.4	7.5	8.2
Density, g/cm^3	1.26	1.34	1.23	1.3	1.26	1.4	1.19	1.29	1.22	1.33
Viscosity, Pa.s	0.101	0.16	0.105	0.134	0.112	0.204	0.107	0.173	0.116	0.195

Notes: WLP codification refers to Binder type and content-Ratio of $TiO_2/CaCO_3$-Storage condition (S: sealed pail and O: opened pail).

* Dosages of thickener, dispersing agent, defoamer, pH regulator, and coalescing agent are given in Assaad (2015).

Five commercially available paint formulations based on VA and PA latexes were produced (Table 1). The VA is a copolymer binder composed of 80% vinyl acetate monomer (VAM) and 20% vinyl ester of versatic acid (VeoVa); it had a white milky appearance with solid content, specific gravity, viscosity, and pH equal to 51.5%, 1.1, 0.085 Pa.s, and 4.5, respectively. The concentration of VA in the produced paints was 15% and 25%. The PA latex is an emulsion polymer designed for gloss and semi-gloss enamels; it had a solid content, specific gravity, viscosity, and pH equal to 47.3%, 1.07, 0.027 Pa.s, and 8.5, respectively. The PA was added at 25% and 35% of the total paint formulation (Table 1).

A rutile grade TiO_2 pigment having specific gravity of 4.05, whiteness larger than 97%, and median particle size of 0.18 µm was used. The extender consisted of $CaCO_3$ having specific gravity of 2.7 and median particle size of 3.4 µm. The TiO_2 was set at either 2.5% or 15%, while $CaCO_3$ adjusted to achieve products having fixed solid content of 45% ± 1%. The VA and PA binders, TiO_2, and $CaCO_3$ particle size distributions determined using laser diffraction analyzer are plotted in Fig. 1 (the cement is also shown in this figure).

The additives including thickener, dispersing, and coalescing agents were adjusted in all paint formulations to achieve similar viscosity levels (Assaad, 2016). A polyether derivative of fatty acids is used as defoamer to break the tiny bubbles formed during paint production. Finally, a solution of 40% sodium hydroxide (NaOH) was used to regulate pH of paints.

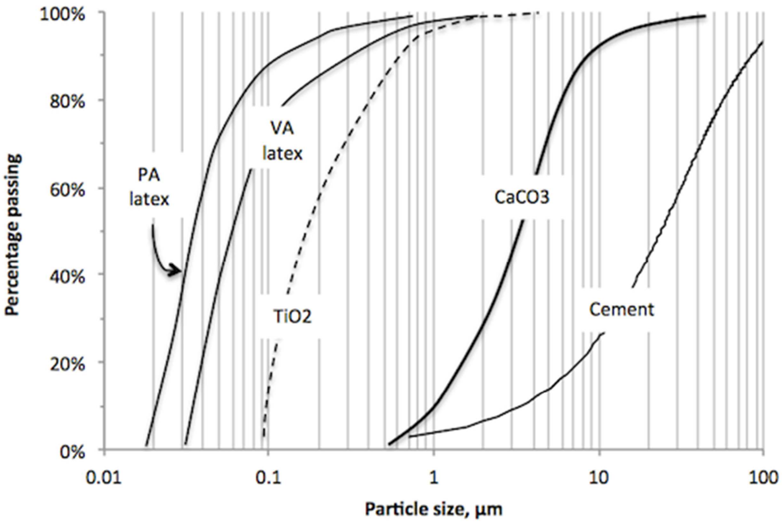

Fig. 1. *Particle size distribution of PA and VA latexes along with the TiO_2, $CaCO_3$, and cement materials.*

2.1.2. Properties of Paints Produced and Storing Conditions

A volume of 20-liters for each formulation was produced; the paint properties determined after production are listed in Table 1. As can be seen, the solid content, pH, and viscosity of all paints were within 45% ± 1%, 9 ± 0.5, and 0.112 ± 0.008 Pa.s, respectively. The density of VA and PA-based paints was within 1.24 ± 0.01 and 1.19 ± 0.01 g/cm^3, respectively. More discussion about the various paint properties including scrub resistance, gloss, and opacity can be seen in Assaad (2015). The WLP codification used refers to binder type and content, ratio of $TiO_2/CaCO_3$, and storing conditions whereby the S and O letters are used for paints stored in sealed (S) or opened (O) pail conditions, respectively.

It is important to note that the produced paints contained no biocides in order to ensure expiry of products (Allsopp et al., 2004; Obidi et al., 2009). Signs of paints expiry typically include sedimentation of solid particles, change in viscosity, decrease in pH, bad odor, and discoloration. In this project, the 20-liters materials produced from each formulation were placed into two pails of 10-liters each, then stored under different conditions. The first pail was sealed and stored in outdoor environment for 6 to 12 months, whereby ambient temperature varied from 18 to 42°C and relative humidity from 45% to 90%. The second 10-liters pail was not sealed, rather kept opened in shadow during the same period of storage time where ambient temperature varied 18 to 32°C and relative humidity from 45% to 70%.

2.1.3. Expiry of Paints and Properties of Resulting WLPs

At end of storage period, all paint pails had musty unpleasant smell and clear fungus spots on top of products. The skin layer that contained fungi was carefully removed, and products vigorously mixed for subsequent testing of solid content, density, pH, and viscosity (Table 1).

In the case of sealed pails, the solid content and density did not considerably vary as these remained within 45.7% ± 0.4% and 1.23 ± 0.04 g/cm^3, respectively. However, pH decreased remarkably from 9 ± 0.5 to 7.8 ± 0.6, which could be attributed to the presence of microbial contaminants (Obidi et al., 2009). Viscosity decreased slightly from 0.112 ± 0.008 to 0.11 ± 0.01 Pa.s.

Pails that were left opened during the storage period were subjected to both bacteria growth and water evaporation (Obidi et al., 2009); the later phenomenon could be associated with relative increase in polymers and particles concentration in the WLP. As a result, considerable increase in solid content, density, and viscosity was noticed. For paints produced using VA binder, those later properties were found equal to 53.7% ± 4.5%, 1.35 ± 0.05 g/cm^3, and 0.17 ± 0.04 Pa.s, respectively, while pH decreased from 9 ± 0.5 to 7.8 ± 0.4 (Table 1). For PA-based WLPs, those properties were equal to 55.7% ± 1.1%, 1.31 ± 0.02 g/cm^3, and 0.185 ± 0.01 Pa.s, respectively, while pH decreased to 8.3 ± 0.1.

2.2. Materials and Mix Proportions for Concrete Testing

2.2.1. Materials

Portland cement conforming to ASTM C150 Type I was used. Its Blaine surface area, median particle size, and specific gravity were 3250 cm^2/g, 26.1 µm, and 3.14, respectively. The cement had C_3S, C_3A, and Na_2O_{eq}. values of 63.5%, 6.1%, and 0.71%, respectively. Continuously graded crushed limestone aggregate and well-graded siliceous sand with 20-mm and 4.75-mm nominal size, respectively, were employed (ASTM C33). The coarse aggregate and sand had fineness moduli of 6.4 and 2.4, respectively, and bulk specific gravities of 2.71 and 2.69, respectively. A naphthalene sulphonate-based HRWR conforming to ASTM C494 Type F was used. It had a solid content, sulfate content, specific gravity, and pH equal to 35.5%, 4.05%, 1.19, and 8.1, respectively.

Deformed steel bars were used to evaluate bond stress-slip behavior of reinforcement embedded in concrete. The steel bars complied to ASTM A615 No. 13 with nominal diameter (d_b) of 12.7 mm; the Young's modulus and yield strength (f_y) were 203 GPa and 428 MPa, respectively.

2.2.2. Concrete Proportions

Typical concrete mix design used for residential construction was considered; it contained 350 kg/m³ cement, 0.55-w/c, and 0.46 sand-to-total aggregate ratio. The HRWR was adjusted at 1.25% of cement mass to achieve slump of 225 mm. This concrete is considered as the control mix.

The effect of WLPs on concrete properties was evaluated by partially substituting mixing water by 5% and 10% WLP. The substitution rates were selected from existing literature (Nehdi and Sumner, 2003; Mohammed et al., 2008; Almesfer et al., 2012; Assaad, 2015), given that increased rates would most likely lead to unacceptably high concrete slump losses. The resulting w/c calculated after deducting the WLP solid content was affected by addition rates and storing conditions. Hence, w/c decreased to 0.537 and 0.525 when WLPs recuperated from sealed pails are added at 5% and 10% rates, respectively. Such w/c values slightly decreased to 0.535 and 0.519, respectively, when WLPs taken from opened pails are used, given the relative increase in solid content.

The concrete mixing procedure consisted of homogenizing the sand and coarse aggregate with half of mixing water, then introducing the cement gradually over 30 seconds. The remaining part of water along with HRWR were then added and mixed for 1 minute. After a rest period of 30 seconds, the WLP was introduced and concrete remixed for two additional minutes. Testing and sampling were made at room temperature of 23 ± 2ºC and 50% ± 5% relative humidity.

2.2.3. Testing Methods

Following the end of mixing, samples of concrete were taken to evaluate initial slump, air content, unit weight, and final setting time as per ASTM C143, C231, C138, and C403 Test Methods, respectively. The slump loss over time was determined after 60 minutes from initial mixing; the fresh concrete was kept in bowl covered with wet burlap during the rest period, and vigorously mixed prior to testing. The fresh concrete mixtures were then filled in 100×200 mm steel cylinders to determine the compressive strength (f'_c), splitting tensile strength (f_t), and static modulus of elasticity (E) as per ASTM C39, C496, and C469 Test Methods, respectively. The procedures for compacting the concrete in cylinders, demolding after 24 hours, curing in water, capping, and testing at 28 days were according to ASTM C192 Practice.

The effect of WLPs on bond stress-slip behavior was tested using the direct bond method; the specimens measured 150-mm diameter and 120-mm height (Fig. 2). The bars were placed vertically in the bottom of molds before casting. The embedded length was 60 mm (5 d_b) and PVC bond breaker with a length of 60 mm (5 d_b) was inserted around the rebar at concrete surface, in accordance with RILEM/CEB/FIB (1970) recommendations. The steel bars were cleaned prior to use, and highly elastic silicon placed between the rebar and PVC tube. The concrete samples were compacted in the molds in a similar manner than the cylinders used for compression, demolded after 24 hours, covered with plastic bags, and allowed to cure at 23ºC for 28 days. The pullout test was performed using a universal testing machine by recording the pullout load of the steel bar at one end with the concrete block being encased in the steel reaction frame, as shown in Fig. 2. The rebar's relative slips to concrete were monitored from measurements of two LVDTs placed at the free and loaded ends of specimen. To minimize eccentricity effects and tangential stresses, neoprene pads were placed between the concrete top surface and reaction frame (Assaad and Issa, 2013).

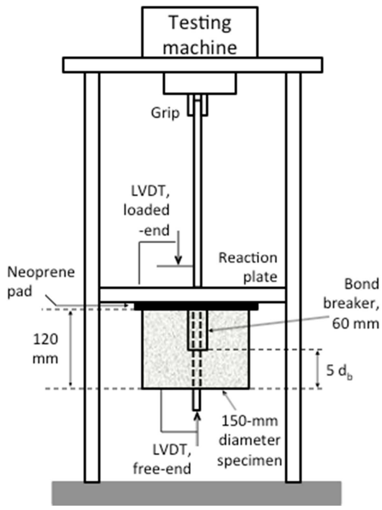

Fig. 2. Schematic of specimen dimensions and set-up for direct bond tests.

3. Test Results and Discussion

The concrete properties obtained following the substitution of mixing water by 5% and 10% WLPs are given in Tables 2 and 3, respectively. During discussion, the variation of any given property determined for concrete containing WLP was normalized with respect to control value, as follows:

$$\Delta(Property), \% = \frac{Property(mix\ containing\ WLP) - Property(control\ mix)}{Property(control\ mix)} \times 100$$

Table 2. Concrete fresh and hardened properties determined when mixing water is substituted by 5% WLPs.

	p/c	Slump, mm		Air content, %	Unit weight, kg/m³	Final setting, min	f'c, MPa	ft, MPa	E, MPa
		T=0 min	T=60 min						
Control mix	0	225	140	3.8	2365	325	31.1	3.88	26.2
15VA-0.68-S	0.1	245	145	4	2355	330	31.8	3.7	25.7
25VA-0.83-S	0.16	230	150	4.2	2380	305	33.2	4.04	26.3
25VA-0.08-S	0.16	240	145	3.6	2345	340	30.9	3.65	26
25PA-0.94-S	0.15	220	140	4.3	2330	330	32	4	26.2
35PA-1.25-S	0.21	210	130	4.6	2350	355	31.5	4.27	25.1
15VA-0.68-O	0.12	235	150	3.7	2360	310	31.8	3.8	26
25VA-0.83-O	0.2	230	135	4.3	2345	315	30.7	3.97	25.2
25VA-0.08-O	0.2	230	145	4.2	2355	340	31	3.9	24.7
25PA-0.94-O	0.18	210	125	3.8	2325	320	30.2	4.37	25.3
35PA-1.25-O	0.25	205	120	4.2	2305	365	30.4	4.82	25

It is to be noted that several mixtures were repeated 3 to 4 times in order to evaluate reproducibility of test responses. The coefficient of variation (COV) is taken as the ratio between standard deviation and mean values, multiplied by 100. Acceptable repeatability was obtained for slump, air content, unit weight, setting time, f'_c, f_t, and E; the corresponding COV was less than 4%, 4.9%, 4.5%, 3.8%, 5.1%, 6%, and 5.9%, respectively. The repeatability of bond properties to embedded steel bars is discussed later in text (section 5).

3.1. Slump and Its Variation Over Time

The effect of WLP constituents, substitution rates, and storing conditions on concrete slump measured right after mixing are plotted in Fig. 3.

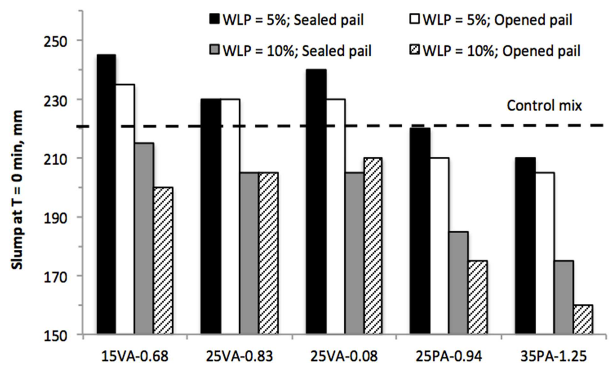

Fig. 3. Effect of WLP constituents, substitution rates, and storing conditions on slump determined right after mixing.

3.1.1. Effect of WLP Constituents

Generally, the use of VA-based WLPs led to slightly improved concrete slump, as compared to equivalent mixtures containing PA-based WLP at similar concentration. For example, the slump decreased from 230 to 220 mm when 25VA-0.83-S and 25PA-0.94-S WLPs, respectively, were added at a rate of 5%. In literature, the change in flow of cementitious materials due to polymer additions has been attributed to the latex nature including its polymerization process and type of surfactant used (Ohama, 1995; Mikanovic et al., 2006). From the other hand, WLPs prepared with higher latex concentration led to reduced slump, due to increased stickiness level. For example, the increase in VA latex concentration from 15% to 25% resulted in reduced slump from 245 to 230 mm, respectively, when 15VA-0.68-S and 25VA-0.83-S WLPs are added at 5% rate.

For WLPs containing given latex type and content, the concrete slump tends to decrease with increased TiO_2 concentration (i.e., higher $TiO_2/CaCO_3$ ratios). For example, such decrease was from 240 to 230 mm for concrete containing 5% of 25VA-0.08-S or 25VA-0.83-S WLPs, respectively. Knowing that TiO_2 particles are much finer than those of $CaCO_3$ (Fig. 1), the decrease in slump could be attributed to increased mixture cohesiveness resulting from higher inter-particle links in the cement matrix (Mohammed et al., 2008; Assaad, 2015).

3.1.2. Effect of Substitution Rates

With some exceptions, the substitution of mixing water by relatively low WLP rate of 5% led to improved slump, as compared to the control mix (Fig. 3). This flowability improvement can be associated to a ball-bearing effect provided by the polymer spherical particles (Ray and Gupta, 1994; Ohama, 1995). Additionally, it is believed that the latex polymers can form electrostatic barriers that hinder flocculation of cement, thus contributing to increased slump (Nehdi and Sunmer, 2003; Assaad, 2015). At higher rates of 10%, however, the slump considerably decreased. For example, such decrease was from 245 to 215 mm for concrete mixtures prepared using 15VA-0.68-S WLP at 5% and 10% rates, respectively. As already explained, this can be related to increased stickiness resulting from higher latex additions, along with a decrease in the amount of free water (i.e., effective w/c) available in the mix.

The relationships between Δ(Slump) determined initially and 60-min later with respect to p/c are plotted in Fig. 4. At p/c less than around 0.15%, positive Δ(Slump) values are obtained, indicating an improvement in workability compared to control mix; but then decreased gradually at higher p/c due to increased stickiness. Nevertheless, it is interesting to note that the rate of Δ(Slump) decrease is particularly accentuated at higher p/c; this increased from −29% to −50% when Δ(Slump) was determined initially or after 60 min, respectively, at p/c of 0.51%. Practically, this suggests that increased WLP additions not only lead to reduced initial slump, but also, the rate of loss over time becomes further pronounced.

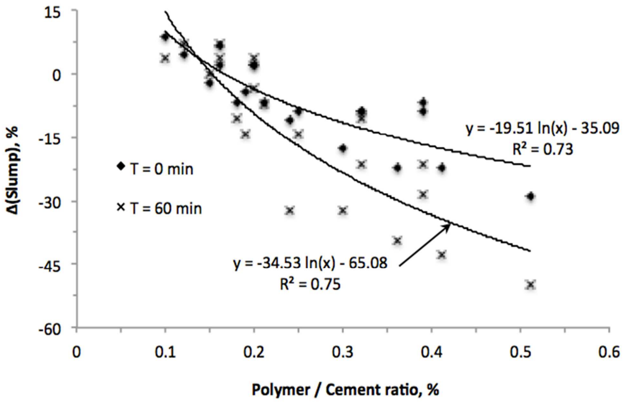

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Fig. 4. Relationships between p/c and Δ(Slump) determined initially and 60-min later.

3.1.3. Effect of Storing Conditions

The slump variations for concrete prepared using WLPs stored in opened pail conditions followed similar trends as those observed when using WLPs stored in sealed conditions (Fig. 3). Hence, the slump decreased with the use of PA latex compared to VA, WLP possessing higher polymer content, and/or higher $TiO_2/CaCO_3$ ratio. However, the extent of slump decrease was particularly accentuated when WLPs stored in opened pail conditions were used. For example, the slump decreased from 245 to 235 mm when 15VA-0.68-S and 15VA-0.68-O WLPs, respectively, were added at 5% rate. For similar WLP constituents, this can be attributed to variations in WLP properties including solid content and viscosity. In fact, pails that were kept opened during the storage period were subjected to water evaporation that increased solid content from 45% to around 54% (for VA-based WLPs) and 56% (for PA-based WLPs), thus reducing the net amount of water in the mix, or w/c. Concurrent to this, the increase in WLP viscosity from 0.11 Pa.s (i.e., sealed pail conditions) to around 0.17 and 0.18 Pa.s (i.e., opened conditions) would lead to increased cohesiveness of interstitial liquid phase, thus contributing to reduced concrete slump.

3.2. Effect WLPs on Air Content and Unit Weight

With few exceptions, the substitution of mixing water by WLP led to increased air content and, consequently reduced unit weight (Tables 2 and 3). The relationships between Δ(Air content) and Δ(Unit weight) with respect to p/c are given in Eq. 1 and 2.

$$\Delta(\text{Air content}) = 89.13(p/c,\ \%) - 6.28$$

Eq. 1 $R^2 = 0.62$

$$\Delta(\text{Unit weight}) = -5.79(p/c, \%) + 0.34$$

Eq. 2 $R^2 = 0.28$

In literature, the inclusion of air bubbles in cementitious materials containing latexes was mainly linked to the presence of surfactants adsorbed onto the surface of polymer particles (Ohama, 1995; Mikanovic et al., 2006). The amount of air entrained depends on the latex type and surfactant's mode of action (i.e., ability to reduce surface tension of water) including its solubility in high pH environments (Mikanovic et al., 2006). As can be seen in Tables 2 and 3, it is hard to draw definite conclusions regarding the effect of WLP constituents (i.e., binder type or pigment/extender ratio) as well as storing conditions on the amount of air entrained.

Table 3. *Concrete fresh and hardened properties determined when mixing water is substituted by 10% WLPs.*

	p/c	Slump, mm		Air content, %	Unit weight, kg/m^3	Final setting, min	f'$_c$, MPa	f$_t$, MPa	E, MPa
		T=0 min	T=60 min						
Control mix	0	225	140	3.8	2365	325	31.1	3.88	26.2
15VA-0.68-S	0.19	215	120	4.5	2340	355	29	3.89	26
25VA-0.83-S	0.32	205	110	4.8	2390	360	28.3	4.61	24.7
25VA-0.08-S	0.32	205	125	4.4	2365	390	25.7	4.27	25
25PA-0.94-S	0.3	185	95	5.3	2315	345	27.1	4.4	25.1
35PA-1.25-S	0.41	175	80	4.6	2290	380	28	4.65	24.2
15VA-0.68-O	0.24	200	95	4.2	2370	330	27	4.18	25
25VA-0.83-O	0.39	205	100	5.2	2315	360	28.1	5.12	23.8
25VA-0.08-O	0.39	210	110	4.8	2325	390	25.9	4.71	25.1
25PA-0.94-O	0.36	175	85	4.9	2290	350	26.5	4.8	24
35PA-1.25-O	0.51	160	70	5.1	2305	420	25.4	5.22	23.2

3.3. Effect of WLPs on Setting Time

Regardless of latex type, concrete incorporating higher WLP substitution rate and/or WLPs containing increased latex concentration exhibited relatively prolonged setting times (Fig. 5). This can be related to the increased percentage of polymer latexes that are adsorbed onto cement grains, thus reducing the rate of cement hydration and resulting in longer setting times (Ohama, 1995; Silva and Monteiro, 2002). The relationship between Δ(Setting time) and p/c is given in Eq. 3.

$$\Delta(\text{Setting time}) = 68.39(p/c, \%) - 10.11$$

Eq. 3 $R^2 = 0.7$

Concrete prepared with WLPs made using increased TiO_2 content (i.e., higher $TiO_2/CaCO_3$ ratio) led to reduced setting times (Fig. 5). For example, such reduction was from 340 to 305 min when the 25VA-0.08-S and 25VA-0.83-S WLPs were used, respectively, at a rate of 5%. Such decrease was respectively from 390 to 360 min when the same later WLPs were used at 10% rate. Mohammed et al. (2008) attributed this phenomenon to the extremely fine TiO_2 particles that could fill additional porosity and act as nucleation sites for the growth of hydration compounds. From the other hand, it is to be noted that the setting times were not remarkably affected by the WLP storing conditions (Tables 2 and 3); also, no conclusion can be made regarding the effect of latex type (i.e., VA vs. PA) on setting time.

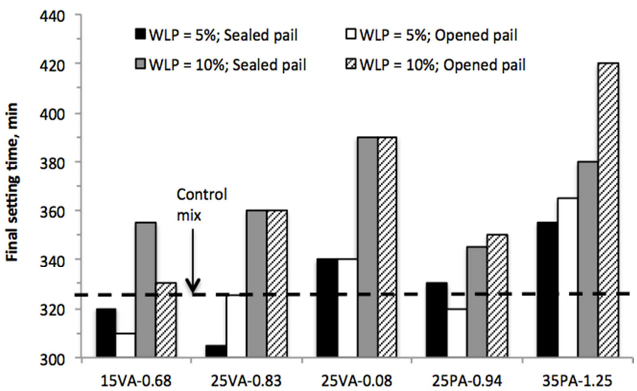

Fig. 5. *Effect of WLP constituents, substitution rates, and storing conditions on setting time.*

3.4. Effect of WLPs on Hardened Concrete Properties

3.4.1. Compressive Strength

The effect of WLP constituents, substitution rates, and storing conditions on f'_c are plotted in Fig. 6. Compared to control mix, a slight increase in f'_c was noted at relatively low WLP rates and/or when WLPs containing reduced latex concentration are used (i.e., low p/c). For example, such increase was from 31.1 MPa for control mix to 33.2 MPa when the 25VA-0.83-S WLP was added at low rate of 5%. In contrast, the use of increased substitution rates and/or WLPs containing higher latex concentrations led to gradual decrease in f'_c.

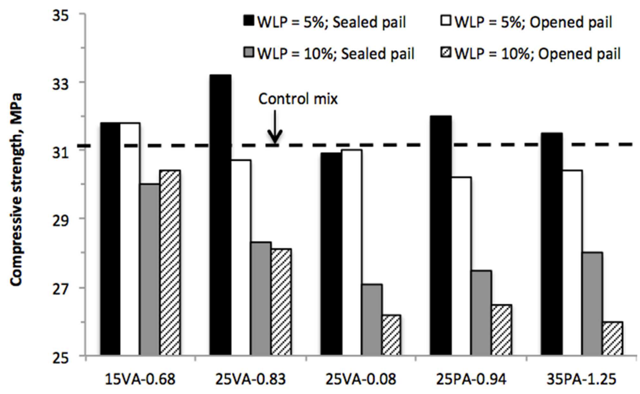

Fig. 6. *Effect of WLP constituents, substitution rates, and storing conditions on 28-days compressive strength*

Such results are in agreement with other findings (Ohama, 1995; Ribeiro et al., 2008; Almesfer et al., 2012), suggesting the existence of a threshold p/c beyond which f'_c is detrimentally affected. Hence, as can be seen in Fig. 7, concrete mixtures formulated using p/c less than around 0.2% did not result in significant f'_c drops; the $\Delta(f'_c)$ ranged from −2.89% to +6.75%. In contrast, f'_c remarkably decreased at higher p/c; this reached −18.3% at p/c of 0.51%. The decrease in f'_c at high polymer contents can be related to a combination of phenomena including delay in cement hydration and increased air content that reduces density of hydrated cement skeleton (Ribeiro et al., 2008). Generally, the VA-based WLPs led to slightly improved f'_c, compared to equivalent mixtures prepared with PA-based WLPs at similar rates.

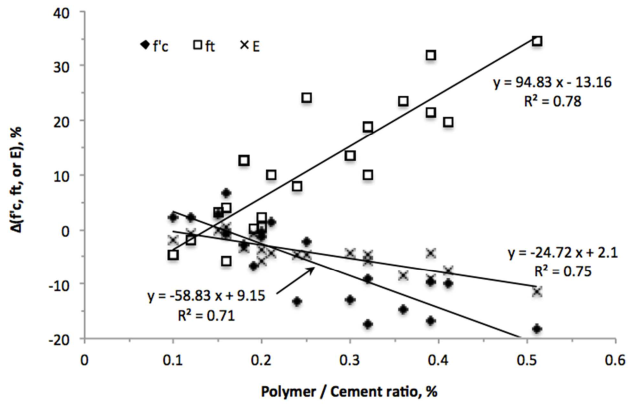

Fig. 7. *Relationships between p/c with respect to $\Delta(f'_c, f_t$, and E) for tested mixtures.*

3.4.2. Splitting Tensile Strength

Unlike f'_c, the f_t increased gradually with p/c (Fig. 7), implying that the concrete tensile strength increases with WLP additions. This can be directly related to the latex polymers that provide increased elasticity through their high tensile strength films, thus bridging the micro-cracks in hardened cement pastes together with stronger interfacial bond with aggregate particles (Ohama, 1995; Ribeiro et al., 2008). The f_t increase is particularly accentuated at high p/c; a value of 5.22 MPa was obtained at p/c of 0.51%, as compared to 3.88 MPa for control mix (i.e., $\Delta(f_t)$ of 34.5%).

Concrete prepared with WLPs containing higher $TiO_2/CaCO_3$ ratios led to increased f'_c and f_t, as compared to those made with equivalent WLPs at lower $TiO_2/CaCO_3$. For example, f'_c increased from 30.9 to 33.2 MPa (and, f_t from 3.65 to 4.04 MPa) when TiO_2 increased from 2.5% to 15%, respectively, for the WLP made with 25% VA and stored in sealed pail condition (Fig. 6). This can be related to the high TiO_2 fineness as compared to $CaCO_3$ (i.e., median size of 0.18 vs. 3.4 µm, respectively), thus reducing porosity and improving denseness of cementitious matrix (Nehdi and Sumner, 2003; Mohammed et al., 2008).

3.4.3. Modulus of Elasticity

The incorporation of WLPs led to reduced E values compared to control mix, reflecting improved elasticity as the result of latex polymer films (Ohama, 1995; Ribeiro et al., 2008). As can be seen in Fig. 7, the decrease in E is proportional to p/c, with relatively acceptable R^2 of 0.75. It is to be noted that the storing conditions did not influence remarkably the development of hardened concrete properties (i.e., f'_c, f_t, and E), as the results obtained remained within the repeatability of testing.

3.5. Effect of WLPs on Bond with Embedded Steel Bars

3.5.1. Repeatability of Responses and Modes of Failure

Table 4 summarizes the bond stress-slip characteristics for control concrete and specimens containing 5% and 10% WLPs stored in sealed conditions; this includes the bond stresses corresponding to slip of 0.01 and 0.1 mm ($\tau_{0.01mm}$ and $\tau_{0.1mm}$, respectively), ultimate bond stress (τ_u) representing the maximum load at failure, and slip at free-end (δ_u) coinciding with the ultimate load. It is to be noted that τ was assumed to be uniformly distributed along the bar's embedded surface; it is given as $\tau = P / \pi\, d_b\, L$, where P and L refer to the load applied and embedded length, respectively (Assaad and Issa, 2013; Metelli and Plizzari, 2014).

The COVs for bond stress-slip characteristics were larger than those obtained for plain concrete properties (f'_c, f_t, and E); this reached 9.4%, 12.8%, 12.2%, and 14.5% for $\tau_{0.01mm}$, $\tau_{0.1mm}$, τ_u, and δ_u responses, respectively. This can be attributed to the coupled dependency of bond results on variations in hardened properties as well as implemented testing procedures such as compaction, bar orientation, and curing. All specimens exhibited a pullout mode of failure characterized by crushing and shearing of the localized embedded region around the bar. No cracks were observed on their external surfaces, indicating that the concrete cover provided adequate confinement (Metelli and Plizzari, 2014). The bond failure occurred at loads less than the bars yielding load, and resulting slips measured at the loaded and free-ends were quite similar.

Table 4. *Bond stress-slip characteristics of WLP-modified concrete to embedded steel bars (WLPs are stored in sealed pail conditions).*

	$\tau_{0.01mm}$, MPa	$\tau_{0.1mm}$, MPa	τ_u, MPa	δ_u, mm
Control mix	1.67	4.3	11.5	1.38
	Concrete containing 5% WLP			
15VA-0.68-S	1.65	4.65	11.6	1.5
25VA-0.83-S	1.8	5.1	12.06	1.47
25VA-0.08-S	1.49	4.17	10.55	1.72
25PA-0.94-S	1.88	4.37	11.7	1.6
35PA-1.25-S	2.01	5.07	10.9	1.71
	Concrete containing 10% WLP			
15VA-0.68-S	2.06	4.8	11.1	1.6
25VA-0.83-S	1.72	4.59	10.7	1.92
25VA-0.08-S	1.8	5.35	11	1.8
25PA-0.94-S	2.14	5.22	9.88	2.16
35PA-1.25-S	2.3	5.51	9.6	2.09

3.5.2. Bond Stress vs. Slip Curves

Typical τ vs. δ curves for concrete incorporating various types and concentrations of WLPs are given in Fig. 8. The control mix prepared without WLP is also shown.

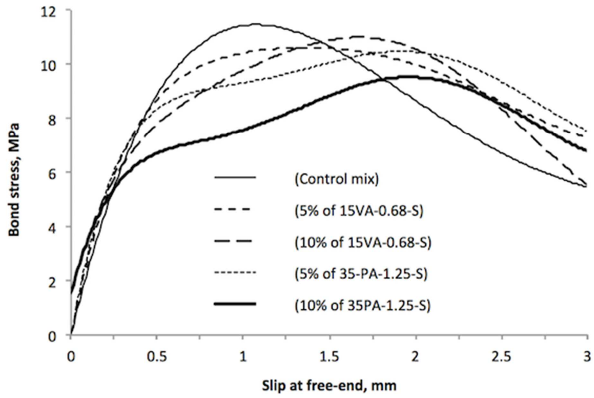

Fig. 8. *Typical τ vs. δ curves for concrete incorporating various types and concentrations of WLPs.*

Behavior of control concrete – Generally, the bond between steel and concrete consists of three mechanisms including adhesion, mechanical interlock, and friction (Makni et al., 2014; Lin and Zhang, 2014). The initial stiffness in the local τ vs. δ relationship is attributed to the adhesive component of bond, and mechanical interlock does not develop until adhesion fails and relative displacement between bar-concrete occurs. The force transfer is thus achieved by bearing of the bar ribs on surrounding concrete, causing the formation of internal cracks and non-linearity of ascending τ vs. δ curves. The mechanical interlock continues until reaching τ_u of 11.5 MPa whereby excessive local slip occurs and concrete between bar deformations shears off. In the post-peak region, only the frictional component of bond remains, and the bond transferred along the bar-concrete interface reduces as the local slip increases (Makni et al., 2014). The corresponding slip at τ_u was equal to 1.38 mm.

Concrete containing WLPs – Regardless of WLP type and concentration, the bars free-end of WLP-modified concrete started to slip at bond stresses higher than those of control mix, thus accentuating the initial stiffness of τ vs. δ curves

(Fig. 8). For example, at the very small slip of 0.01 mm, $\tau_{0.01mm}$ increased from 1.67 MPa for control concrete to 2.01 and 2.3 MPa with the addition of 5% or 10% 35PA-1.25-S WLPs, respectively. This can be attributed to the latex polymers that increase the adhesive component in the elastic region and result in increased interfacial shear stresses between the reinforcing bar and surrounding concrete. This phenomenon was also noticed when using virgin latexes; it was explained by the presence of electrochemically active polymer-cement co-matrixes at the interfaces with reinforcing bars, thus relaxing the stresses during loading and retarding the friction-controlled slip of rebars (Chen and Chung, 1997; Wang et al., 2012).

When the adhesive component of bond fails, the responses of ascending curves until reaching τ_u gradually softened and resulting τ_u decreased with WLP substitution rates; i.e., from 11.5 MPa for control concrete to 10.9 and 9.6 MPa at 5% and 10% 35PA-1.25-S rates, respectively. The corresponding δ_u increased from 1.38 to 1.71 and 2.09 mm, respectively. This can be explained by the nature of this test during which the bond to steel is affected by the properties of surrounding concrete that is placed in compression (i.e., mixtures containing increased WLP rates are characterized by lower E and f'_c). In other words, the softening of ascending curves due to WLP additions is the result of more pronounced compressive strain-softening phenomenon due to the presence of polymer latexes (Liu and Wang, 2003; Wang et al., 2012). From the other hand, the decrease in τ_u is in agreement with that of f'_c, given that the induced compressive concrete-bar stresses at failure are affected by the bearing capacity of surrounding concrete that is placed under compression.

3.5.3. Effect of p/c and WLP Consitutents on Bond Characteristics

The relationships between p/c and $\Delta(\tau_{0.01mm}$, τ_u, and $\delta_u)$ are plotted in Fig. 9 (the $\tau_{0.1mm}$ are not shown, as these are less relevant due to WLP additions). As can be seen, concrete made using higher p/c (i.e., increased WLP rates and/or WLPs containing increased latex polymers) led gradually to higher $\tau_{0.01mm}$ values. This suggests that the adhesive component of bond including the interfacial shear stresses between bar-concrete could be improved with WLP additions; such improvement reached 38% at 0.41% p/c. From the other hand, $\Delta(\tau_u)$ showed slight increase when p/c was lower than around 0.2%, which is in agreement with the threshold p/c found earlier for f'_c. Above this threshold, $\Delta(\tau_u)$ decreased until reaching a value of −16.5% at p/c of 0.41%. It is to be noted that no clear conclusions can be drawn regarding the effect of latex type (i.e., VA vs. PA) on the magnitude of $\tau_{0.01mm}$ and τ_u values.

With some exceptions, concrete incorporating WLPs containing increased TiO_2 percentages led to increased τ_u measurements. For example, τ_u increased from 10.55 to 12.06 MPa when TiO_2 increased from 2.5% to 15%, respectively, for concrete containing 5% of 25VA-0.08-S and 25VA-0.82-S WLPs, respectively. This can be related to a combination of phenomena including reduced porosity and improved denseness of cement paste that strengthen the transition zone adjacent to the reinforcing bars (Gomes et al., 2005). Additionally, the increased fineness of TiO_2 particles are expected to reduce bleed water, which contributes to increased concrete bearing strength around the steel bars.

The slips at failure shifted gradually towards higher values with increased p/c (Fig. 9); at the highest p/c of 0.41%, $\Delta(\delta_u)$ reached 52%. Practically, this indicates that the structural ductility of reinforced concrete members tends to increase with WLP additions, which could be of particular interest for high-strength concrete where splitting failure most likely occurs abruptly.

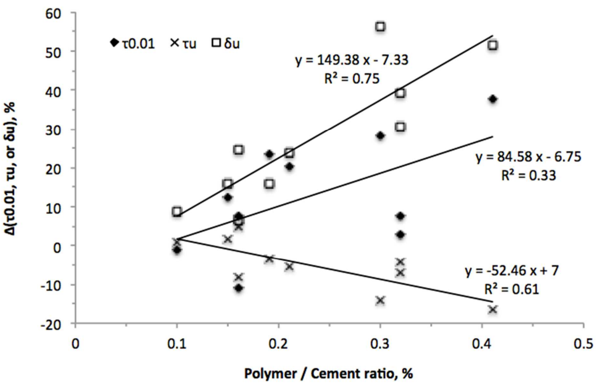

Fig. 9. *Relationships between p/c with respect to $\Delta(\tau_{0.01mm}$, τ_u, and $\delta)$ for tested mixtures.*

4. Conclusions

This paper is part of a comprehensive research project undertaken to evaluate feasibility of recycling WLPs during concrete production with value added. From the foregoing results, the following conclusions can be warranted:

(1) Concrete slump measured after mixing decreases with the addition of WLPs containing PA-based latex, higher $TiO_2/CaCO_3$ ratio, increased WLP substitution rate, and/or WLPs stored in opened pail conditions. The rate of slump loss over time is affected by p/c that influences stickiness of concrete.

(2) Air content and unit weight for concrete containing 5% WLPs were quite close to those determined on control mix. The increase in WLP rate to 10% led to higher air content, given the surface tension modification at the cement/polymer interface.

(3) Concrete containing WLPs made using higher latex contents (or, p/c) as well as higher substitution rates led to prolonged setting times. This was related to increased percentage of polymer latexes that are adsorbed onto cement grains, thus reducing the rate of hydration process. The setting times tended to decrease with higher $TiO_2/CaCO_3$ ratio, given the fine TiO_2 particles that act as nucleation sites for the growth of hydration compounds.

(4) Compared to control mix, gradual decrease in f'_c was noted at high WLP rates of 10% and/or when WLPs

containing increased latex concentration are used (i.e., high p/c). This was related to a combination of phenomena including delay in cement hydration and increased air content that reduces density and strength of hydrated cement skeleton.

(5) Unlike f'_c, the f_t increased gradually with p/c, given the presence of latex polymer films that provide increased elasticity through their high tensile strengths. From the other hand, the incorporation of WLPs led to reduced E values, reflecting improved elasticity. Concrete prepared with WLPs containing higher $TiO_2/CaCO_3$ ratios led to higher f'_c and f_t.

(6) The bars embedded in WLP-modified concrete started to slip at higher bond stresses than control concrete, thus accentuating the adhesive component of bond. Afterwards, the responses of τ vs. δ curves gradually softened until reaching τ_u; those later values were found to decrease with increased p/c. The slips at failure shifted gradually towards higher values with increased p/c, suggesting improved ductility of tested specimens.

(7) Concrete incorporating WLPs containing increased percentages of TiO_2 led to increased τ_u, given the reduced bleeding and improved denseness of cement paste that strengthens the transition zone adjacent to reinforcing bars.

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