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Preparation and characterization of a water-based nanoparticle green polymer intended for application as a protective concrete coating against carbonation

Youssef L. Nashed[1*], Fouad Zahran [2] , Mohamed Adel Youssef[2]

[1] Research and development department, Eagle chemicals company, Egypt.
[2] Faculty of Science, Helwan University, Helwan, Egypt.

Abstract

This study investigates the effectiveness of anti-carbonation coatings based on nanoemulsion terpolymers used in protecting reinforced concrete structures from concrete carbonation. A nano styrene acrylate terpolymer that a surfactant had stabilized was produced via free radical emulsion polymerization. The eco-friendly emulsion is confirmed using minimum film-forming temperature, Fourier transforms infrared spectroscopy and particle size distribution. It is then formulated as a binder for water-based anti-carbonation coating. Elongation, crack-bridging ability, low carbon dioxide permeability, average pull-off adhesion strength, and QUV/weathering are the characteristics of the anti-carbonation coating. Finally, we compared the prepared anti-carbonation coating based on the formulated nanoemulsion terpolymers as a binder with the commercial styrene acrylate copolymer coating in anti-carbonation terms. The produced coating based on the formulated emulsion was shown to perform better than its commercial counterpart, according to the data obtained. The nano styrene acrylate emulsion was shown to boost anti-carbonation coating performance. The prepared coating based on synthetic nanoemulsion terpolymers increases the life span of the concrete and prevents the collapse of buildings, among other significant and social implications.

Keywords: nanoemulsion terpolymers, Coating, Anti-Carbonation, Concrete, Corrosion.

1. Introduction

Around the world, reinforced concrete is frequently used to build structures in various industries. These structures need to be shielded from aggressive chemicals to extend their lifespan. Despite multiple corrosive influences, the concrete construction is designed to remain durable. Steel corrosion in concrete is generally brought on by some ailments, such as cracking and carbonation, in concrete structures [1,2]. Concrete carbonation is a chemical process that occurs when carbon dioxide (CO2) in the air interacts chemically with byproducts of cement hydration. A weak carbonic acid is produced when atmospheric carbon dioxide dissolves in pore water. This acid then dissociates, combines with calcium hydroxide, and reacts with calcium silicate hydrates (CSH) to produce water and calcium carbonate (scheme 1demostrate the carbonation reaction). Without a doubt, these actions reduce the alkalinity of the concrete [2]. During the diffusion process known as carbonation, CO2 is transported from one place to another by random molecular mobility. Steel bars corrode mostly because of carbonation, which leads to structural damage in concrete. Steel reinforcing bars inserted into concrete are generally shielded from corrosion under normal conditions by the surrounding concrete's high alkalinity. Steel could no longer be passivated at a pH of 9.5, according to [3]. But the carbonation event reduces the alkalinity of the concrete from around 12 to less than 9, depassivating the steel reinforcement and leaving it vulnerable to corrosion [4,5,6].
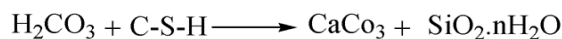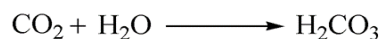
$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCo_3 + 2H_2O$$

$$H_2CO_3 + C\text{-}S\text{-}H \longrightarrow CaCo_3 + SiO_2.nH_2O$$

Figure 1: demonstration of the carbonation reaction.
Aquick and easy technique to stop and slow down the carbonation of steel buried in concrete is to apply an anti-carbonation coating over the cleaned surface of

the concrete. This method's steel in concrete should be corrosion-free for around ten years [7].

Surface treatments may be used on newly constructed structures as a preventative measure, on already-built structures where the need for future protection is anticipated, and on structures that are being repaired to increase their lifespan. For concrete, there are four basic categories of surface treatments that can be distinguished. Continuous organic films that serve as coatings. Cementation layers, treatments that fill the capillary pores, and hydrophobic treatments that line the surface of the pores [8,9,10,11,12].

They have two effects: first, they decrease the permeability of aggressive compounds in the concrete, and second, they lower the water content of the concrete, which in turn lowers the electrical conductivity of the concrete as well as the corrosion rate. By creating a continuous polymer film with a thickness of 0.1 to 1 mm on the concrete surface, organic coatings are frequently employed to prevent the infiltration of carbon dioxide. A few millimeters thick, usually less than 10 mm, a low permeability layer is created by cementing coatings. Because of their low modulus of elasticity, coatings typically have strong adhesion, good flexibility, and significant crack-bridging ability. They have extremely low porosity and limited water permeability as a result. They often exhibit sufficient water vapor permeability and decent breathability as well. Since no significant pressures at the concrete/coating contact would cause delamination or breaking of the coating, water vapor can escape from the concrete without doing so. Additionally, its substantial number of inorganic materials ensures strong resistance to ultraviolet light (UV). In cracked concrete, they are highly advised since they enable the cracks to be sealed and their protective effect to be sustained for a very long period [9,13,14].

This work uses a mixture of monomers (Styrene, Methyl methacrylate, 2-Ethylhexyl acrylate, acrylic acid, and acrylamide) from Sigma-Aldrich Company, USA). Sodium dodecylbenzene sulfonate (SDBS) (Sigma-Aldrich Company, USA) was used as an anionic surfactant. TergitolNP30 (Dow chemicals company, USA) was used as a nonionic surfactant. Were used to formulate the nanoemulsion terpolymers [15]. Utilizing the nanoemulsion terpolymers as a green polymer, where water is the main carrier solvent [16]. Since cracks and

carbonation are the two main factors contributing to carbonation which leads to steel corrosion in concrete, this study aims to improve coating against both. Nanoemulsion terpolymers-prepared anti-carbonation coating was compared to commercial coating.

2. Materials & Experimental
2.1 Chemical materials.
Styrene, Methyl methacrylate (both are hard monomers that give the emulsion rigidity, water, and block resistance), 2-Ethylhexyl acrylate (soft monomer that provides the emulsion with the elasticity, elongation, and cracks bridging ability), acrylic acid, and acrylamide(both are water soluble monomer enhance polymerization to avid grit formation) were supplied from Sigma-Aldrich Company, USA. sodium dodecylbenzene sulfonate (SDBS) (Sigma-Aldrich Company, USA) were used as anionic surfactants. TergitolNP30 (Dow chemicals company, USA) was used as a nonionic surfactant. Ammonium persulfate (APS) (Sigma-Aldrich Company, USA) was an initiator. Ammonium hydroxide (El-Nasr Chemicals Company, Egypt) was used as a pH stabilizer. Titanium dioxide (under the trade name Cristal 128, Cristal KSA) was used as the main pigment. Texanol 2, 2, 4-trimethyl-1, 3-pentanediol monoisobutyrate (Eastman Chemical Company, USA). Propylene glycol (Eastman Chemical Company, USA) was used as coalescing agent. An anti-foaming agent used is agitan301 (MünzingChemie, Germany). the antibacterial agent is Acticide HF purchased from THOR, and the associative thickener used is acrysol™ ase-60 Thickener (DOW, Germany.

2.2. Polymerization method.
2.2.1. preparing a pre-emulsion.
In a glass beaker fitted with a high-speed homogenizer (Ultra-Truax homogenizer), distilled water, ionic surfactant, and monomers were added for 30 min. Acrylamide and acrylic acid were added as the mixture was continuously homogenized.

2.2.2. Procedure for polymerization.
Polymerization was conducted in a 1 L stainless steel reactor equipped with a reflux condenser, thermometer, and mechanical stirrer. Homogenization and polymerization occurred at temperatures of 25 and 80

°C, respectively. The following steps are included in the process:

1. In the mentioned amount in table 1(monomer mixture) from de-ionized water, a pre-emulsion including styrene, 2-EHA, acrylic acid, and acrylamide was emulsified by (SDBS) and homogenized for 30 minutes at a speed of 1000 rpm (25°C).

2. Mix the amount in table 1(initiator mixture) from de-ionized water with the initiator (APS).

3. 5% of the pre-emulsion was added to the reactor along with deionized water and nonionic surfactant NP30, and it was stirred for 15 minutes at 80 °C using a low-speed mechanical agitator (100 rpm). An additional 15 minutes were given to allow for micelle development.

4. After that, in 175 minutes, the pre-emulsion was fed to the reactor using a dropping funnel.

5. The initiator solution was continuously dropped into the reactor in steps 3 and 4.

6. After adding all materials, polymerization was allowed to continue for 3 hours, and any free monomer was removed by keeping the reactor at 80 °C for an hour.

7. The pH of the reactor was then brought down to 8 by adding ammonia solution and cooling it to 30 °C. After neutralization, the latex was given a biocide addition before being filtered through a 100-mesh filter and collected. Table 1 displays the nanoemulsion terpolymers synthesis's formulation [16,17,18,19].

Table 1: The formulation for nanoemulsion terpolymers

Raw material	Weight %
Initial reactor charge	Ter-polymer (St/MMA/EHA)
De-ionized water	37.5
NP30-non-ioinic surfctant	0.5
Monomer mixture (4 hr feed)	
De-ionized water	9
SDBS	3.0
Styrene	5.4
Methyl methacrylate	10.6
2-Ethyl hexaylacyrlate	34.0
Acrylic acid	2.0
Acrylamide	0.5
Initiator mixture (4 hr feed)	
APS(initiator)	0.3
De-ionized water	6.5
Post Additives	
Acticide HF	0.1
Anti-foaming agent	0.1

Figure 2: Chemical structure of nanoemulsion terpolymers.
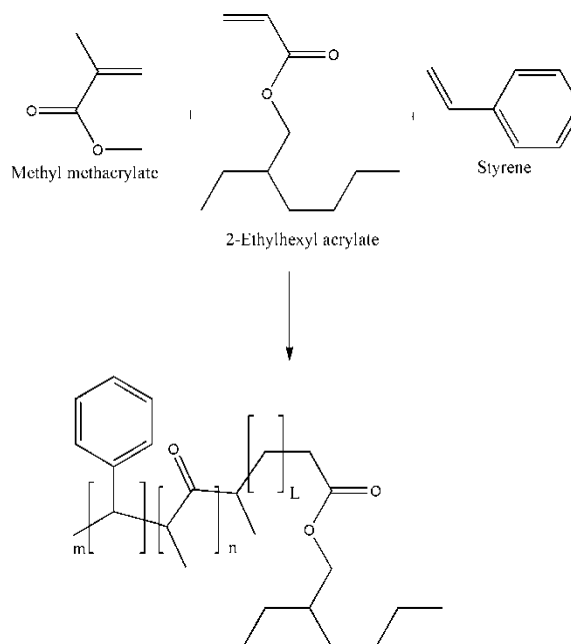
2.2.3. Method of preparation of anti-carbonation coating.

The preparation of the two-stage anti-carbonation coating, mill base, and letdown is listed in Table 2. The effectiveness of nanoemulsion terpolymers as a binder in a waterborne anti-carbonation coating was assessed and compared to commercial coating. A high-speed mixer with an operating range of 3000 rpm is required to produce latex paints. The specified amount of water was added where the thickening and dispersing agents had previously been added. The mixer was run at 900 rpm. The remaining pigments and filler were selectively incorporated. After that., 45 minutes were spent with the mixer running at 2750 rpm (round per minute). Finally, the mixer speed was lowered, and the nanoemulsion terpolymers emulsion was slowly added to achieve complete formulation homogenization [17].

3. Characterization of the prepared emulsion:

To characterize latex and dried latex film and gather in-depth data from trials, qualitative and quantitative impressions of the emulsion polymerization process were collected as follows:

3.1. Fourier transforms infrared (FT-IR).

Functional groups produce distinctive bands in terms of intensity and position, which IR spectroscopy utilizes to identify structures (frequency). The dried samples' polymer composition was, by FT-IR analysis, identified. The

instrument used had an FT-IR spectrum, PerkinElmer 100, USA, between 4000 and 400 cm^{-1}.

3.2. Minimum film formation temperature (MFFT).

It was detected by Rho-point MFFT 60-bar, UK, ASTM D 2354.

3.3. Particel size distrubation PSD.

Using a Malvern, UK-based Mastersizer 3000 Basic guide, the produced polymers' particle size and particle size distribution were evaluated. The hydrodynamic size in the region of 10 nm to 3.5 mm was measured using this device. The number of distinct particle size measurements was determined by averaging the results of the experiments.

3.4. Viscosity measurement.

By Brookfield Viscometer based on (ISO 2555-2018; 23°c) Sp5, Rpm 20.

3.5. Determination of Non-Volatile Matter Content.

(Solid Content) based on ISO 3251-2019.

Table 2: The formulation for anti-carbonation coating.

Raw material	Weight %	Function
Mill base		
Water	18.0	Solvent
Acticide HF	0.2	Biocide
Under stirring 900 rpm.		
Tylose HEC 100.000	0.3	Thickener
WD-EAGLE(AS4/40)45%	0.3	Dispersing agent
Agitan301	0.2	Anti-foaming agent
Ammonia	0.2	pH stabilizer
Cristal128	20.0	Pigment
Calcium carbonate five μm	10.0	Filler
Talc 20 μm	5.0	Filler
Micro Mica 160 μm	0.50	
Grind for 45 minutes at 2750 rpm.		
Let down/after that, reduce the mixer to 900 rpm.		
Binder	40.0	
Agitan301	0.2	Anti-foaming agent
Acticide HF	0.2	Biocide
Texanol	0.4	Coalescing agent
Glycol	0.4	Co-solvent
Dibutyl phthalate (DBP)	0.8	Plastisizere
Acrysol™ ase-60	0.3	Rheological additive
Water	3.0	Solvent

4. Charaization of anti-carbonation coating based on nano styrene acrylate terpolymer emulsion as the binder.

4.1. Elongation at break %.

The sample was molded and prepared according to ASTM D412-06A for Vulcanized Rubber and Thermoplastic Elastomers, tested by Universal Tester Instron 3367, USA. This test is to characterize the elasticity of the prepared coating.

4.2. Crack-bridging ability.

It was carried out using a test method following BS EN 1062-7: 2004 and a sample preparation standard per BS EN 1766: 2017.
Nature of Substrate: Concrete
Dry film Thickness: 150±50 μm
Substrate dimension: 75*50 mm
Test method: A
Room temperature: 23°C
Relative humidity: 55%
This test was carried out in EPRI labs.

4.3. Carbon dioxide permeability.

It was evaluated using a test procedure that adhered to BS EN 1062-6: 2002.
Nature of Substrate: Concrete
Dry film Thickness: 150±50 μm
Room temperature: 23°C
Relative humidity: 55%
Classification of coating material and coating: C1
This test was carried out in EPRI labs.

4.4. Average pull-off adhesion strength.

It was carried out using an ASTM 4541-17-compliant test technique.
Dry film Thickness: 150 μm
Nature of Substrate: Concrete
Test method: type 5 self-aligning tester.
Room temperature: 23°C
Relative humidity: 55%
Test position: vertical.
After seven days of curing, the test was carried out between old concrete and an intelligent care repair bond. This test was carried out in EPRI labs.

4.5. QUV/weathering.

According to ASTM-G154, the QUV weathering tester analyzed the accelerated weathering test. The materials were evaluated in a QUV cyclic UV

weathering tester (120 V, 60-Hz model made by the Q Panel Company, USA), exposed to aging for 200 hours. Observational visuals were created, and any odd observations were recorded.

5. Results & Discussion:

One of the main causes of concrete degradation in reinforced concrete is carbonation, which happens when ambient carbon dioxide (CO_2) lowers concrete's alkalinity and makes it more susceptible to assault from water and oxygen. Concrete spalling is a result of steel corroding. This work focuses on creating an anti-carbonation coating using a nano styrene acrylate terpolymer emulsion as a binder because commercial coatings do not shield steel from corrosion caused by carbonation.

5.1. Results of the prepared emulsion.
5.1.1. Fourier transforms infrared (FT-IR).

The FTIR spectrum of the nanoemulsion terpolymers produced by emulsion polymerization is shown in Figure 3. As clearly seen, C-H aromatic stretching between 3100 and 3000 cm^{-1}, C-H aliphatic stretching at 2958 and 2870 cm^{-1}, C=O pulling at about 1730 cm^{-1}, the strong absorptions at 1641 cm^{-1} due to skeletal C-C aromatic stretching, C-O and C-C stretching at 1161, 1119, 1070, 1065, and 950 cm^{-1}, aromatic C-H out-of-plane bending around 697 cm^{-1}. Moreover, the peak at 1161 cm^{-1} is related to the C-O-C stretching vibration of the ester group. The CH_2 deformation vibration bands are observed at 1450-1382 cm^{-1}[20-21]. The NH2 group of acryl amide shows a peak at 3400 cm^- [20].
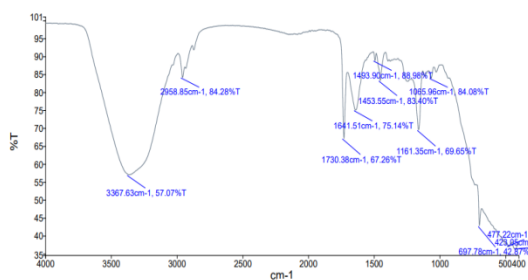

Figure 3: IR chart for the prepared emulsion.

5.1.2. Minimum film formation temperature (MFFT).

The MFFT is zero, indicating that the polymer has elastic properties due to the combination of the monomers [22].

5.1.3. Dynamic light scattering.

Particle size has an impact on the physical stability of emulsions directly. Reduced particle size lets more particles be distributed on the boundary, yielding a more stable emulsion. The emulsion samples were measured in the particle size and size distribution tests. The PSD chart of the nano Ter-polymer is shown in Figure 4. The average diameter of the nano Ter-polymer was calculated as 0.02 nm with 90% of the sample and 0.0720 μm with 50% of the model [23].
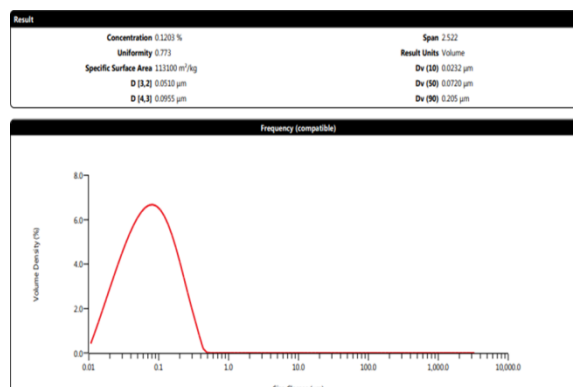

Figure 4: PSD (particle size distribution for prepared emulsion.

5.1.4. Viscosity and nonvolatile Content for the prepared emulsion.

The result is listed in table 3.

Table 3: analysis of the prepared emulsion.

Test	Test Method	Unit	Result
Viscosity by Brookfield	(ISO 2555-2018; 23˚C) sp5, rpm 20	cP	1000
Nonvolatile content (%)	ISO 3251-2019	%	51.0
MFFT	ASTM D 2354	˚C	0.0

5.2. Results of anti-carbonation coating based on nano styrene acrylate terpolymer emulsion as the binder.

5.2.1. Elongation at break %.

As shown in Figure 5, a commercial coating sample ruptures before it reaches 100% of its length. Additionally, we found that the anti-carbonation coating created from nano styrene acrylate terpolymer emulsion has an elasticity that enables it to stretch up to 800% longer than the length of the original sample, aiding in adhesion to concrete and blocking the entry of acid gases [24].
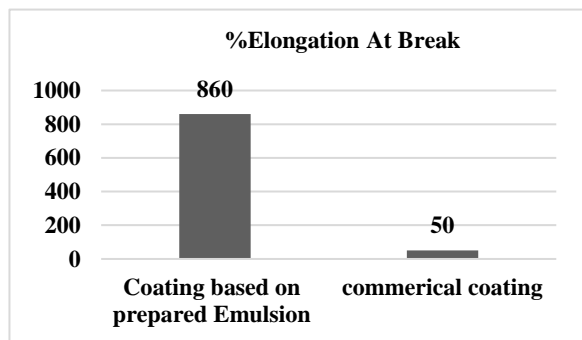
Figure 5: Elongation at break % curve.

5.2.2. Crack-bridging ability.

Crack-bridging ability refers to the ability of the anti-carbonation coating to cover cracks created in the concrete substrate while maintaining the properties and reducing the likelihood of cracks spreading and causing deterioration. The protective layer's flexibility and kind are key factors in its capacity to bridge cracks: Polymer-cement coatings have excellent fracture bridging capabilities, making this treatment appropriate for application on damaged supports. The created anti-carbonation coating samples, developed using a nano-styrene acrylate terpolymer, showed a fracture width at the first failure of 2.5 mm. In contrast, commercial paint showed a crack width at the first failure of 0.7 mm, as shown in Figure 6 [25,26,27].
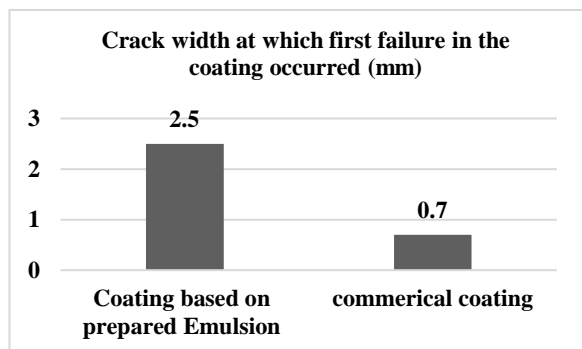

Figure 6: crack-bridging ability curve.

5.2.3. Carbon dioxide permeability.

Figure 7 shows the CO_2 permeating through the substrate. Using a nano-styrene acrylate terpolymer with a permeability of 0.2 gm/m^2day and commercial coating results revealed a 54 gm/m^2day permeability through the samples. The size and quantity of interlayer distances in the created binder were reduced by combining a monomer in the developed emulsion, which inhibited carbon dioxide penetration. Additionally, the ester

groups in the carbon skeleton made the compound more electrically negative, which caused a high carbon dioxide repulsion [28].
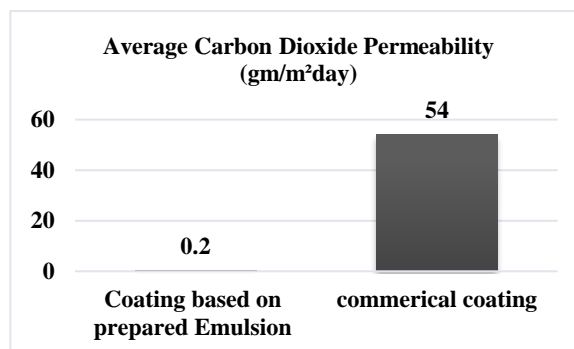

Figure 7: **carbon dioxide permeability curve.**

5.2.4. Average pull-off adhesion strength.

Figure 8 shows the results of the pull-off adhesion. Using coating based on the nano-styrene acrylate terpolymer with a pull-off strength of 2.15 N/mm^2 and commercial coating results revealed a 1 N/mm^2. The adhesion on the concrete substrate resists and prevents the penetration of the acid gases, which are the main causes of the carbonation which leads to steel corrosion.
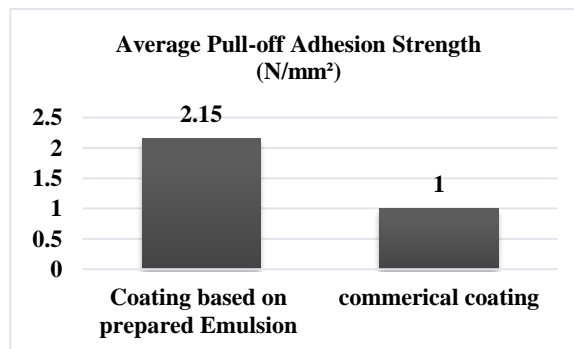

Figure 8: average pull-off adhesion strength curve.

5.2.5. QUV/weathering.

There were no remarkable cracks or observations of shapes. This provided proof that the nano-styrene acrylate terpolymer-based anti-carbonation covering was stable. Because MMA only slightly absorbs light and UV rays, it has a high QUV/weathering resistance. The energy required to dissolve the molecular bonds inside the substance is absent from the modest amount of absorbed radiation. As a result of this peculiar quality, polymers with long-term weather and crack resistance are mainly well-investigated [17,29,30].

6. Conclusion.

The study aimed to develop new latexes with good elongation, crack-bridging ability, low carbon dioxide permeability, average pull-off adhesion strength, and resistance to ultraviolet light and weathering. A suitable feeding strategy, Tg, and improved dry latex film characteristics were used to manufacture latexes. By employing three monomers—Styrene, 2-Ethylhexyl acrylate, and Methyl methacrylate—conventional seeded emulsion polymerization was used to create nano Styrene acrylate terpolymers. We were able to create stable latex with enhanced physicomechanical characteristics. FTIR, PDS, and thermal analyses were used to characterize the produced latexes (TGA). More stable colloidal dispersions were obtained using surfactant mixes, which combine an anionic surfactant with a nonionic surfactant. Formulating an anti-carbonation coating with this emulsion and comparing it to a commercial coating in the following terms:

6.1. Elongation at break %:

A commercial coating sample ruptures before it reaches 100% of its length, as seen in Figure 5. Furthermore, we discovered that the anti-carbonation coating made from nano styrene acrylate terpolymer emulsion has an elastic property that enables it to stretch up to 800% longer than the length of the original sample, assisting in adhesion to concrete and preventing the entry of acid gases like CO_2 which is the main cause for carbonation.

6.2. Crack-bridging ability:

When a concrete substrate develops cracks, the anti-carbonation coating has the potential to bridge those cracks, preserving the concrete's qualities and lowering the risk that they would spread and deteriorate the structure. Commercial paint displayed a crack width at the first failure of 0.7 mm. In contrast, the anti-carbonation coating samples, made using a nano-styrene acrylate terpolymer, displayed a fracture width at the first failure of 2.5 mm, as shown in Figure 6.

6.3. Carbon dioxide permeability:

Figure 7 depicts the CO_2 leaking through the substrate. A nano-styrene acrylate terpolymer with a permeability of 0.2 gm/m^2 day and commercial coating showed a 54 gm/m^2 day permeability through the samples. Combining a monomer in the established emulsion prevented carbon dioxide penetration and decreased the size and number of interlayer gaps in the created binder.

6.4. Average pull-off adhesion strength:

The outcomes of the pull-off adhesion are depicted in Figure 8. Commercial coating studies showed a pull-off strength of 1 N/mm^2 when coating based on the nano-styrene acrylate terpolymer, which has a pull-off strength of 2.15 N/mm^2. The concrete substrate's stickiness resists and blocks the entry of acid gases, which are the primary causes of carbonation and steel corrosion.

From the results mentioned above, we can conclude that coating based on the prepared nano-styrene acrylate terpolymers performs better than the commercial coating in the main terms of anti-carbonation coating elongation, crack-bridging ability, low carbon dioxide permeability, average pull-off adhesion strength, and QUV/weathering.

Conflict of interest:

No conflict exists, and the authors declare that they have no conflict of interest.

Reference

1. Gagg C. R.; Cement and concrete as an engineering material: An historic appraisal and case study analysis, Engineering Failure Analysis 40, 114-140 (2014). https://doi.org/10.1016/j.engfailanal.2014.02.004.

2. Torgal F. P., Miraldo S., Labrincha J.A., and De Brito J. "An overview on concrete carbonation in the context of eco-efficient construction: Evaluation, use of SCMs and/or RAC." Construction and Building Materials 36, 141-150 (2012), https://doi.org/10.1016/j.conbuildmat.2012.04.066.

3. Hobbs, D. W., Carbonation of concrete containing pfa, Magazine of concrete research 40.143, 69-78 (1988), https://doi.org/10.1680/macr.1988.40.143.69.

4. Elsayed E. M., Ashraf E., Abdelbasir S. M., Rashad M. M., and El-Shamy A. M., Fabrication, Characterization and Monitoring the Propagation Of Nanocrystalline ZnO Thin Film On Ito Substrate Using Electrodeposition Technique, Egyptian Journal Of Chemistry, 2022, -. Doi: 10.21608/Ejchem.2022.126134.5595

5. Ashraf M. E., Farag H. K., and Saad W., Comparative Study of Removal of Heavy Metals from Industrial Wastewater Using Clay and Activated Carbon in Batch and Continuous Flow Systems. Egyptian Journal of Chemistry, 60, 6, 1165-1175 (2017). doi: 10.21608/ejchem.2017.1606.1128.

6. Ashraf M. E., Fabrication of Commercial Nanoporous Alumina by Low Voltage Anodizing. Egyptian Journal of Chemistry, 61, 1, 175-185 (2018). doi: 10.21608/ejchem.2017.2189.1175

7. Park, D. C., Carbonation of concrete in relation to CO2 permeability and degradation of coatings, Construction and Building Materials 22.11, 2260-2268 (2008). https://doi.org/10.1016/j.conbuildmat.2007.07.032.

8. Swamy, R. N., and S. Tanikawa. An external surface coating to protect concrete and steel from aggressive environments, Materials and structures 26.8, 465-478 (1993).

9. Swamy N., and Arvind K., Suryavanshi and Shin Tanikawa, Protective Ability of an Acrylic-Based Surface Coating System Against Chloride and Carbonation Penetration into Concrete-ACI Materials Journal 95.2 (1998).

10. McGrath, P. F., A simple chamber for accelerated carbonation testing of concrete, Available online: https://www. xypex. com. au/file/10310/284 (accessed on 15 August 2018) (2016).

11. Shehata M., El-Shafey S., Ammar N., and El-Shamy A.M., Reduction of Cu+2 and Ni+2 Ions from Wastewater Using Mesoporous Adsorbent: Effect of Treated Wastewater on Corrosion Behavior of Steel Pipelines, Egyptian Journal of Chemistry, 62, 9, 1587-1602 (2019). doi: 10.21608/ejchem.2019.7967.1627

12. Moatamed M. M., Youssif M., and El-Shamy A.M., Selective formula as a corrosion inhibitor to protect the surfaces of antiquities made of leather-composite brass alloy, Egyptian Journal of Chemistry 63.12, 5269-5287 (2020).

13. Sergi, G., Seneviratne A. M., Maleki M.T., Sadegzadeh M.M., and Page C. L., Control of reinforcement corrosion by surface treatment of concrete, Proceedings of the Institution of Civil Engineers-Structures and Buildings 140.1, 85-100 (2000). https://doi.org/10.1680/stbu.2000.140.1.85

14. Seneviratne, A. M. G., G. Sergi, and C. L. Page. "Performance characteristics of surface coatings applied to concrete for control of reinforcement corrosion." Construction and Building Materials 14.1 (2000): 55-59.DOI:10.1016/S0950-0618(00)00011-8.

15. El-Sayed N., Aisha N., Mun G. A., Iskakov R., Irmukhametova G. S., and Sakhy M., Preparation and characterization of acrylic primer for concrete substrate application, International Journal of Polymer Science (2016). https://doi.org/10.1155/2016/1754168.

16. Yin X., Li L., Pang H., Luo Y., and Zhang B., Eco-friendly functional two-component flame-retardant waterborne polyurethane coatings: a review, Polymer Chemistry (2021).https://doi.org/10.1039/D1PY00920F.

17. Abd El-Wahab H., Attia M., Hassan W. H., and Nasser A. M., Preparation, characterization and evaluation of some acrylate polymers nanoparticles as binder to improving the physical properties of water-based paints, Int. J. Nanopart. Nanotechnol 5, 2-18 (2019).

18. Abd El-Wahab, H., and Hassan W. A., Preparation and characterization of nano-copolymers (styrene/2-Ethyl hexyl acrylate) based on two different surfactants and use it as a binder for surface coatings, Nano Tech Nano Sci Ind J 12.2, 127 (2005).

19. El-Sherif H. M., Nasser A. M., Hussin A. I., Abd El-Wahab H., Ghazy M. B. M., and Elsayed A. E., Nano emulsion binders for paper coating synthesis and application, Journal of Macromolecular Science, Part A 54.5, 271-287 (2017). https://doi.org/10.1080/10601325.2017.1294450.

20. Prakash N. J., Pradsad S. H., Nehru S., Sathish M., and Soundararajan S., Synthesis Characterization and Testing of Emulsion Polymerized Vinyl Acetate – Acrylamide Copolymers for Bio-Degradable Applications, Journal of Polymer and Textile Engineering 1, 04-11 (2013).

21. Huang, Tao, and Gong S., Preparation of Emulsifier-Free Styrene–Acrylic Emulsion via Reverse Iodine Transfer Polymerization, Polymers 13.19 (2021): 3348.DOI: 10.3390/polym12030730.

22. Learner, and Tom, Analysis of modern paints. Getty publications, 2004.

23. Ibrahim, Yousif H.E., Regdon, G., Kristó, K., Kelemen, A., Adam, M.E., Hamedelniel, E.I., and Sovány, T., Design, and characterization of chitosan/citrate films as carrier for oral macromolecule delivery, European Journal of Pharmaceutical Sciences 146 (2020): 105270.

24. Tadros, and Tharwat F., Emulsion formation, stability, and rheology, Emulsion formation and stability 1, 1-75 (2013).

25. Haloi, Dhruba J., Naskar K., and Singha N. K., Modification of Chlorinated Poly (propylene) via Atom Transfer Radical Graft Copolymerization of 2-Ethylhexyl Acrylate: A Brush- like Graft Copolymer, Macromolecular Chemistry and Physics 212.5, 478-484 (2011). https://doi.org/10.1002/macp.201000506.

26. Re G., Croce A., Angelo D., Marchese L., Rinaudo C., and Gatti G., Application of nano-coating technology for the protection of natural lapideous materials, Surface and Coatings Technology 441, 128507 (2022) .https://doi.org/10.3390/ma14133719.

27. Delucchi, M., and G. Cerisola., Influence of temperature on crack-bridging ability of coatings for concrete, Progress in Organic Coatings 75.3, 253-258 (2012). https://doi.org/10.1016/j.porgcoat.2012.05.006.

28. Tommy Y. L., Liao W., Wong C. K., and Tang W., Evaluation of carbonation resistance of paint-coated concrete for buildings, Construction and Building Materials 107, 299-306 (2016). https://doi.org/10.1016/j.conbuildmat.2016.01.026.

29. Osswald T.A., International plastics handbook: the resource for plastics engineers. Hanser Gardner Pubns. (2016).

30. Campo, and Alfredo E., Complete Part Design Handbook. Munich, Germany: Hanser, (2006).