

Absorbency and Corrosion Inhibition Property of Polyamide Epoxy and Superabsorbent Polymer Composite Material

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Polyamide epoxy containing superabsorbent polymer (SAP) was investigated for its absorbency property and its application in the inhibition of corrosion in carbon steel. The type of SAP was sodium polyacrylate with relatively low crosslinking density. Fine particles of SAP was mixed with epoxy resin and subsequently the polyamide hardener was added allowing the polymerization of epoxy resin to occur while the SAP is dispersed within the polymer matrix. Prior to this, the SAP used for this application was examined in terms of its absorbency property in pure water and in sodium chloride solutions. The composite material, i.e. cured epoxy with SAP, was likewise examined for its absorbency property. Results showed decreased absorbency of pure SAP in sodium chloride solution compared with pure water, and the same trend was exhibited in the composite material but with much lower absorbency. The composite material was applied on the surface of carbon steel of 40 mm x 100 mm and thickness of 0.7mm and tested for anticorrosion property. The composite material gave better results than the control material of polyamide epoxy without SAP. The better corrosion resistance exhibited by the composite materials could be attributed to the self-healing property of SAP.

1. Introduction

One of the applications of Superabsorbent Polymer (SAP) that is gaining more attention lately is in the prevention of material oxidative degradation, and it takes advantage of SAP's ability to function as a smart polymer. Generally, oxidative degradation refers to reaction of organic materials in the presence of oxygen. Elevated temperatures, heat, and catalysts, such as metals and metal ions, assist in oxidation (Zweifel H, 1998). Material degradation becomes even worse at some weathering situations acting concurrently on the material, such as rainfall or condensed water acting on photodegraded surface caused by sunlight (Woo et al., 2013). Moisture and UV radiation have been identified as environmental factors that affect the properties of polymer-based composite materials the most. In marine environment, for example, the problems associated with water logging are particularly compounded by the salinity of the environment and hastens its oxidative decomposition (Martin et al., 2012). Normally, the oxidative degradation of a polymer-based material can be prevented by restraining the exposure of the material to environments containing oxygen and moisture (Chairul et al., 2012). One approach to tackle the problem of oxidative degradation of a polymer-based material is through the application of SAP, and this study focuses on this.

SAP's are known for attracting and absorbing large amounts of water. These polymers have three-dimensional structures consisting of hydrophilic networks of cross-linked polymer chains which can absorb and retain large amounts of water and other various forms of fluids even under some degree of pressure (Yawen et al., 2019, Melendres et al. 2019). When dry superabsorbent polymers are immersed in water, they swell but do not dissolve to maintain its rigidity (Omidian et al., 1998, Melendres and Carillo, 2019). The swelling property of SAP with higher gel strength at swollen state makes SAP suitable as a self-healing material for application on inhibition of oxidative degradation. Jud and Kaushch (1979) studied the self-healing behavior of different types of thermoplastics where self-healing of the polymeric materials was found to be attributable to surface adhesion. Dry (1996) had applied the concept of self-healing to

cementitious materials to improve cement matrix permeability and repair cracks. Trask and Bond (2007) had extended this study to polymeric materials where self-healing of the materials studied was mainly due to surface adhesion. Several researches had utilized SAP in concrete for self-healing of cracks (Seongwoo et al., 2019, Jianhui et al., 2020). Harn et al. (2019), investigated the efficacy of three self-healing approaches, namely biochar-immobilized bacteria, SAP, and a combination of PVA and steel fibers, to heal concrete subjected to damage.

Corrosion is an example of oxidative degradation which pertains to the oxidation reaction of metal surface when exposed to harsh environment. The high cost of corrosion affects numerous industries, domestic applications and public sectors worldwide and highlights the need for improved corrosion measures (Deepak et al., 2017). Carbon steel, one of the most widely used construction materials had received numerous studies on corrosion prevention due to its low corrosion resistance. Barrier protection are generally used for the protection of carbon steel wherein organic coatings have been applied on the metal surface to promote oxygen and moisture deprivation (Yuanyuan et al., 2015). These coatings provide a dense barrier against a corrosive environment, however these materials normally do not protect underlying metal when the coating gets damaged and the substrate are exposed to the harsh environment. This research aims to utilize the property of SAP to self heal in order to address this problem. Although several researches had been done utilizing SAP as component of polymeric coating materials (Akihiro and Kazuma, 2012; Fan et al., 2018), research involving polyamide epoxy as coating medium with SAP has not yet been thoroughly explored. Epoxy resin with Bisphenol A diglycidyl ether (BADGE) as its main component with polyamide as the curing agent is widely used as anti-rust paint (Nelly et al., 2016, and Bagherzadeh et al., 2007). It is the objective of this study to produce a composite material comprising of this epoxy material with added SAP into its polymerized structure and investigate its application as coating onto carbon steel. A simple method of corrosion test of carbon steel using high impedance voltmeter with Ag/AgCl as the reference electrode was employed where the samples were exposed to 3% NaCl for a specified period of time.

2. Materials and Methods

2.1 Materials

The SAP's were imported from China, Shandong Tongli Co., Ltd, tightly sealed to maintain moisture below 5%. Analytical grade sodium chloride from Avantor Performance Materials, Inc. was used for preparing the sodium chloride solution. These types of SAP were prepared by polymerizing neutralized acrylic acid with difference in the amount of crosslinkers. Deionized water with conductivity of $<5 \mu\text{S/cm}$ was used for the tests. The epoxy resin and the curing agent polyamide were obtained from Polymer Products Philippines.

2.2 Methods

Particle Size Analysis

The particle size analysis of SAP was determined using Zeiss Axio Scope A1 microscope. The Feret diameter method was used to determine size of the particles. A particle counter detects and counts particles and the results are reported automatically using a software.

Preparation of Composite Material, Substrates and Application

A specified amount of SAP is dispersed in epoxy resin using a mechanical stirrer to evenly distribute the SAP. Stirring continues and the curing agent is then added to maintain even distribution of the SAP within the polymerizing epoxy matrix. All preparations are carried out at room temperature of around 28°C . The resulting mixture is immediately applied on the surface of carbon steel with size of 100 mm length x 40 mm width x 0.70 mm thickness. The carbon steel plates are previously cleaned by grinding the surface with abrasive paper to remove rust and then cleaned with ethanol before coating application. Coating application is carried out using a $\frac{1}{2}$ inch wide paint brush. All curing is done for 24 hours. Three layers are applied where the top and bottom layers are plain cured epoxy while the middle layer is a composite material of SAP and epoxy. A 20mm long artificial coating defect is produced on the coated steel surface by making a scratch using a sharp knife before the sample undergoes corrosion testing.

Absorption Test for SAP

Two methods were used to determine the absorption capacity of SAP: the free swell capacity, and the absorption under pressure. A tea bag method is used to measure the free swell capacity (FSC). Absorption under pressure (AUP) is determined by placing a load of 21 g/cm^2 , consisting of a cylindrical piston, on the SAP constrained inside a cylinder but permitted to absorb the test solution.

In both methods, absorption capacities are evaluated by determining the weight before and after test solution absorption. Absorption capacity of SAP in composite materials was evaluated with free swell method.

SEM-EDX Characterizations

Samples of composite material with SAP were sputtered with thin layer of gold coating under vacuum before being analyzed under an SEM equipped with Oxford Instrument X-Max for Energy Dispersive X-Ray analysis (EDX).

Corrosion Test of Coated Samples

A small plastic tube of 25 mm diameter was placed onto the coated carbon steel specimen enclosing the scratched length and was sealed at the outer circumference to make it leak tight. A test solution of 3% NaCl solution is prepared and poured into the tube. The potential of the metal electrode is measured with respect to a standard Ag/AgCl electrode using a Fluke 287 high impedance voltmeter with the positive terminal connected to the metal specimen and the negative terminal connected to the reference electrode.

3. Results and Discussion

3.1 Particle Size Evaluation

Photos of SAP particles taken during particle size determination are shown in Figure 1 for SAP-1 and SAP-2. Both SAP's, as shown in the photos, have irregular shapes. SAP-1 has fewer number of particles with size $>50 \mu\text{m}$ than SAP-2 for the same area taken, as shown in Figure 1, indicating that the former has a larger particle size than the latter. Its measured feret average diameter of $158.21 \mu\text{m}$ is larger than that of SAP-2 which has a feret average diameter of $96.57 \mu\text{m}$. Details of the particle size distribution are shown in Table 1. These are the results of each SAP three deminations for SAP-1 and SAP-2 having 95.96% accurarcy.

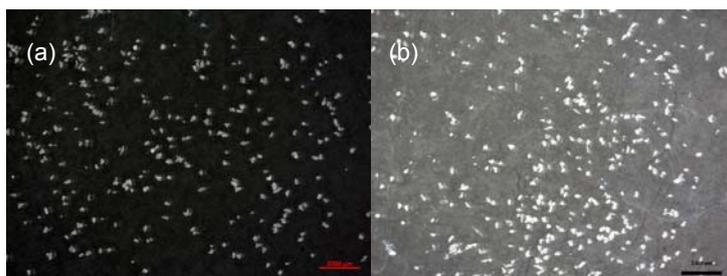


Figure 1. Photos of (a) SAP-1 and (b) SAP-2 taken under a Zeiss Axio Scope A1 microscope during the particle size analysis of SAP particles using a Feret diameter method.

Table 1: SAP Particle Size Details

Items	SAP-1	SAP-2
Count	480	1177
$<50\mu\text{m}$ (%)	46.25	67.2
$>50\mu\text{m}$, $<300\mu\text{m}$ (%)	30.51	12.19
$>300\mu\text{m}$ (%)	23.24	20.61
Feret Average Diameter (μm)	158.21	96.57

3.2 Absorption Test Results of SAP

The absorption capacities decreased with increasing concentration of NaCl, the lowest value of which was obtained at 3% NaCl, roughly the concentration of NaCl in seawater. Although SAP absorbs large amounts of pure water, its absorption capacity decreased when NaCl is present in the electrolyte solution - a typical absorption behavior of SAP (Buchholz and Graham, 1998). At a concentration of 3%, the free swell capacity of SAP decreased to 32.12 g/g and 37.11 g/g from absorption capacities of 324.26 g/g and 399.40 g/g with pure water for SAP-1 and SAP-2, respectively. Standard deviations for these tests with 5 samples each, range at 3.0 - 6.5. SAP-2 has higher free swell capacity than SAP-1 for all the concentrations of NaCl tested and at pure water. In the same manner, the absorption under load decreased with increasing concentration of NaCl. At a concentration of 3%, the absorption under load of SAP decreased to 9.60 g/g and 8.12 g/g for SAP-1 and SAP-2, respectively. Standard deviations for these tests with 5 samples each range at 1.0 - 3.4.

The observed difference in the values of FSC and AUP could mainly be attributed to the difference in the amount of crosslinkers used.

Table 2: The absorption capacities of SAP

% NaCl	Free Swell Capacity, g/g		Absorption Under Pressure, g/g	
	SAP-1	SAP-2	SAP-1	SAP-2
0	324.26	399.40	78.23	67.23
0.5	52.12	73.75	26.10	24.12
1.0	42.10	59.67	21.41	19.34
3.0	32.12	37.51	9.60	8.12

3.3 Evaluation of Composite Materials

Table 3 shows the basis weight of different layers of coatings for both SAP-1 and SAP-2 at different % of SAP with respect to the epoxy resin. With increased % SAP in the middle layer, the thickness of the overall coating increased as well, however SAP-2 gave thinner coating than SAP-1 which could be explained in terms of the difference in the particle size of the two SAP's as shown in Table 1. No delamination of the coating for the

Table 3: Coating Basis Weight and Thickness

% SAP	Coating Basis Weight, g/m ²				Coating Thickness, mm	
	Bottom Layer	Middle Layer	SAP	Top Layer	SAP-1	SAP-2
0	188	188	0	188	0.41	0.38
5	188	195	6.6	188	0.52	0.47
10	188	202	13.9	188	0.56	0.52

specimens containing SAP was detected and its adhesion property is similar with the control. The absorption capacities of SAP within the composite material at 3% NaCl was found to be 24.45 g/g and 23.45 g/g for SAP-1 and SAP-2, respectively. The observed values are lower than that of pure SAP shown in Table 2 which can be attributed to the binding effect of epoxy to SAP.

Results of SEM EDX of Composite Materials

Figure 2 shows the SEM image and EDX analysis of the hardened polyamide epoxy with SAP incorporated in its polymerized structure. The elemental composition from the EDX analysis indicates the presence of important elements of SAP in the matrix of the cured epoxy, such as sodium, confirming SAP's incorporation in the structure of polyamide epoxy.

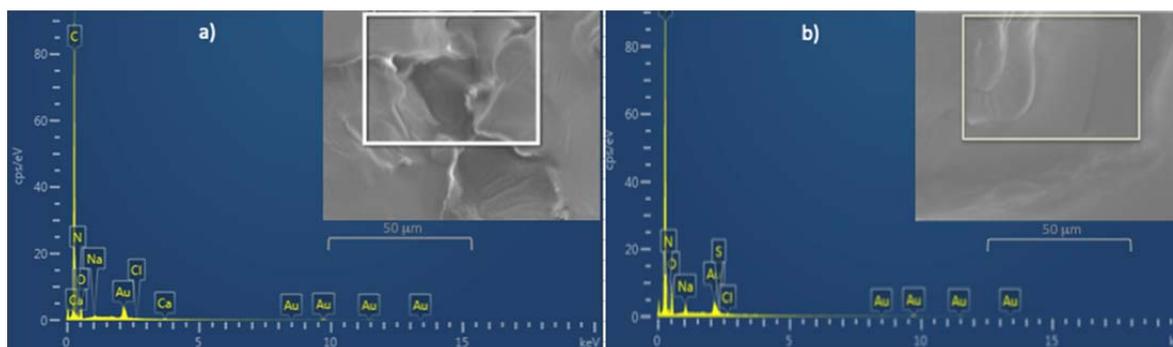


Figure 2. Absorption Under Load of superabsorbent polymers (SAP-1 and SAP-2), 10% SAP.

Corrosion Test Results

Figure 3 shows microscopic photos of the scratch area of specimens with artificial defects after 24 hours of exposure in 3%NaCl solution. Figure 3(a) refers to microscopic photo of specimen without SAP, which is the control specimen for this experiment. As seen in the photos, rusts are formed at the scratched portion of the control specimen as indicated by the brown staining of the area. Figure 3(b) and Figure 3(c) refer to microscopic photos of the scratched portion of the coated samples with 10% SAP content in the composite material of the middle layer for SAP-1 and SAP-2, respectively.

For these samples, no visible brown staining can be observed demonstrating that no perceivable rusting occurred. Similarly, no visible rusting occurred for specimens with 5% SAP under the same exposure condition.

The specimens coated with the composite material containing SAP-1 and SAP-2 demonstrated greater resistances to corrosion, as shown in Figure 3. Based on the corrosion potential monitoring results presented in Figure 3, this resistance to corrosion could likely be attributed to the suppression of the anodic reaction, as shown by the general shift of the corrosion potential to more noble values for samples coated with SAP-composite material. If this interpretation holds true, SAP-1 specimens exhibits better anodic reaction inhibition than SAP-2 specimens, likely due to the higher absorption capacity under pressure of SAP-1. The particle size of SAP-1 may contribute to its better suppression of corrosion due to its homogeneity, as the too small particle size of SAP-2 increases the likelihood of agglomeration of SAP, being too hygroscopic, particles giving rise to its inhomogeneity within the polyamide epoxy matrix. Furthermore, specimen with 10% SAP concentration gives better tendency to inhibit corrosion than the one with 5%, obviously due to the higher capacity for absorbing water and a faster gelling response, although SAP much greater than 10% could result to inferior performance as less water may be able to penetrate due to permeability problem. The likely inhibition of SAP of the anodic process described above could be attributed by the formation of a film at the scratched portion as water is absorbed by SAP, resulting to swelling and covering of the defect to a large extent, and isolating the carbon steel surface from the environment. This protective film is somewhat visible in the microscope photos of the scratch in Figure 3. This response of SAP of swelling and covering the damaged (scratched) portion of the coating can be considered as a self-healing process, and causes the suppression of corrosion in the coating defect area. .

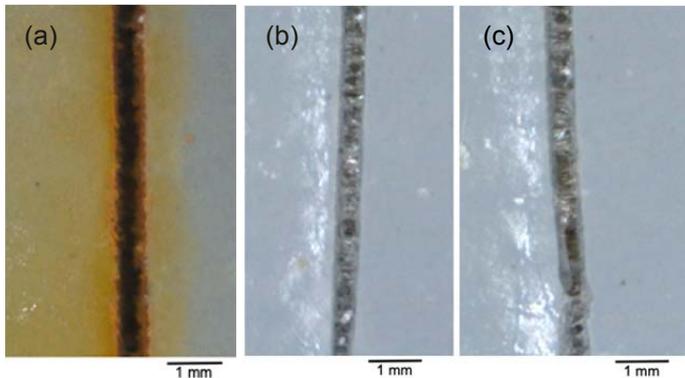


Figure 3. Scratched portion of specimens after 24-hour exposure at 3% NaCl: (a) control; (b) 10% SAP-1; and, (c) 10% SAP-2.

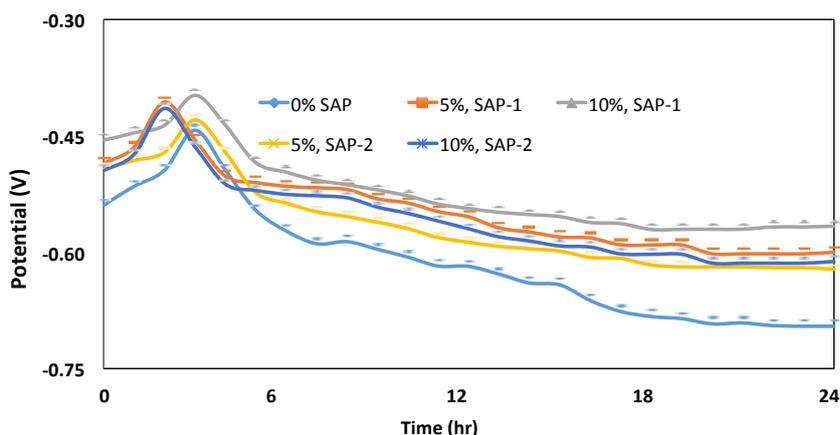


Figure 4. Corrosion potential monitoring for carbon steel coated with composite material of varying amounts of SAP.

4. Conclusions

A composite material composed of polyamide epoxy and SAP was applied as coating material for carbon steel. Two types of SAP with different absorption properties were examined in terms of the free swell and absorption under load. While SAP-1 gave lower free swell capacity than SAP-2, its absorption under load is higher. SEM and EDX analyses showed the incorporation of SAP within the matrix of the polyamide epoxy. Samples of carbon steel of size 100 mm length x 40 mm width x 0.7 mm thickness coated with composite material were scratched using a sharp knife to produce a coating defect of specified length and then immediately exposed to 3% sodium chloride solution. Based on the microscopic photos of the samples and the results of corrosion potential monitoring, the composite material embedded with SAP in its structure was able to control corrosion of the carbon steel likely via a mechanism of anodic reaction control

References

- Akihiro Y. Kazuma O., 2012, Self-healing coatings using superabsorbent polymers for corrosion inhibition in carbon steel, *Corrosion Science*, 59, 258-262.
- Buchholz, F.L., Graham, A. T., 1998, *Modern Superabsorbent Polymer Technology*. Wiley-VCH, New York.
- Chairul I.S., Ghani S.A., Khair M.S.A., Thayoob, Y.H.M., Ghazali Y.Z.Y., 2012, Kraft paper insulation's life assessment and effects of oxygen and moisture to paper insulation's deterioration rate, *Power and Energy (PECon)*, 2012 IEEE International Conference, doi: 10.1109/PECon.2012.6450311on, 728-731.
- Deepak D., Katerina L, Thomas B., 2017, Carbon steel corrosion: a review of key surface properties and characterization methods, *RSC Adv.*, 7, 4580-4610.
- Dry C., 1996, Procedures developed for self-repair of polymer matrix composite materials. *Compos. Struct.* 35, 263-269.
- Emilie D., Nelly D., Bernard B, Sylvain C., 2016, Improved cardanol derived epoxy coatings, *Progress in Organic Coatings*, 91, 9-16.
- Fan Z., Pengfei J., Mengqiu P., Dawei Z., Yao H., Guoliang L., Xiaogang L., 2018, Self-healing mechanisms in smart protective coatings: A review, *Corrosion Science*, 144, 74-88.
- Harn W. K., Souradeep G. A., Anastasia N.A., Wil V.S., 2019, Biochar-immobilized bacteria and superabsorbent polymers enable self-healing of fiber-reinforced concrete after multiple damage cycles, *Cement and Concrete Composites*, 100, 35-52.
- Jianhui L., Kamal H. K., Caijun S., 2020, Effect of superabsorbent polymer characteristics on rheology of ultra-high performance concrete, *Cement and Concrete Composites*, 12, 103636.
- Jud K., Kausch H.H., 1979, Load transfer through chain molecules after interpenetration at interfaces. *Polym. Bull.* 1, 697-707.
- Lee X.H.D., Wong H.S., Buenfeld N.R., 2016, Self-sealing of cracks in concrete using superabsorbent polymers, *Cement & Concrete Research*, 79, 194-208.
- Melendres A., Antang J.A. and Manacob J., 2019, Investigation of Superabsorbent Polymer Absorbency at Reduced Chemical Potential of Water, *MATEC Web of Conferences*, 268, 04010.
- Melendres, A. V., Carillo, L. A., 2019, Surface Treatment of Superabsorbent Polymer with Corn Starch for Improved Properties, *Asean J. Chemical Engineering*, 19, 66-73.
- Omidian H., Hashemi H.O., Sammes P.G., Meldrum I., 1998, A model for the swelling of superabsorbent polymers, *Polymers*, 39, 6697-6704.
- Roberge P. R., 2019, *Handbook of Engineering Corrosion*, McGraw Hill Education.
- Seongwoo G., Eunjong A., Myoungsu S., 2019, Self-healing of modified sulfur composites with calcium sulfoaluminate cement and superabsorbent polymer, *Composites Part B: Engineering*, 469-483.
- Trask R.S., Williams G.J., Bond I.P., 2007, Bioinspired self-healing of advanced composite structures using hollow glass fibres, *J. Roy. Soc. Interface*, 4, 363-371.
- Woo R.S.C., Kim J.K., Leung C.K.Y, Chen Y.H., Zhu H.G., Li J., 2007, Environmental degradation of epoxy-organoclay nanocomposites due to UV exposure. Part I: Photodegradation, *Compos Sci Technol*, 67, 3448-3456.
- Yawen T., Huaxin C., Zhendi W., Cheng X., Rui H., 2019, Performances of Cement Mortar Incorporating Superabsorbent Polymer (SAP) Using Different Dosing Methods, *Materials*, 12, 1619, doi:10.3390/ma12101619.
- Yuanyuan Q., Yongxin L., Scott J., Nicholas S., Yida F., Xianming S., 2015, The Application of Anti-Corrosion Coating for Preserving the Value of Equipment Asset in Chloride-Laden Environments: A Review, 10, 10756 – 10780.
- Zweifel H., 1998, *Principles of oxidative degradation: Stabilization of Polymeric Materials, Macromolecular Systems Materials Approach.*, Springer, Berlin, Heidelberg.