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Box-Behnken method for enhanced performance of solvent-based epoxy coatings reinforcement with diatomite/surfactant/zinc borate

İrem Toprakçı[1] & Nil Acaralı*,[2]

[1]Istanbul University-Cerrahpasa, Department of Chemical Engineering, 34320, Avcılar-Istanbul, Turkey

[2]Yildiz Technical University, Department of Chemical Engineering, 34210, Esenler-Istanbul, Turkey

E-mail: nilbaran@gmail.com

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This study is aimed to improve the properties of the organic coatings by adding additives of various properties to industrial organic coatings with epoxy resin and to obtain organic coatings with superior properties. Boron end-product, methacrylate-based fluorinated liquid and diatomite additives have been added to the epoxy resin-containing organic coatings in the specified proportions (0-6% (w/w)). The Box-Behnken optimization method has been applied on the metal surface. The surfaces where the organic coatings are applied are subjected to various tests (adhesion, corrosion etc.) in accordance with the standards. According to the test results, coatings are resistant to impact, corrosion, high adhesion resistance, gloss and covering values. In addition, as a result of Thermogravimetry/Differential Thermal Analysis (TG/DTA), flame retardancy is improved, more homogeneous structures are obtained by adding additives with Scanning Electron Microscopy (SEM) analysis, hydrophobic property is improved according to the contact angle and surface free energy measurement results. Consequently, it has been observed that additives added to the organic coatings in various proportions improve the organic coating in terms of flame retardancy, surface properties and hydrophobicity. It is envisaged that the organic coatings with new properties can be preferred in different industries.

Keywords: Box-Behnken, Coating, Diatomite, Epoxy, Zinc borate

Main purposes of organic coatings are to protect, decorate and identify both objects and materials[1]. Degradation can occur in alltypes of materials but mostly in metallic materials due to corrosion[2]. Corrosion of metals brings structural failures and this situation causes large economic setbacks in varied industries[3]. One of the most important tasks of the developers is to research and develop new type of organic coating, which constitutes very high ratio of overall costs of measures for corrosion controlling[4]. Epoxy resin coatings properties such as high bonding strength, remarkable corrosion resistance and fine adhesion gives them the ability of providing a barrier metal matrix against corrosive medium, thus epoxy resin coatings can protect possible intrusion of corrosive substances[5]. Natural hydrophilicity of epoxy resin is very effective against long-term anticorrosion activity and this ability widely overlooked. For increasing the life length of corrosion protection, enhancing epoxy coatings' hydrophobic abilities is major concern and purpose of the scientists this past years[6]. Zinc borate may be classified as a boron-based compound and can act as flame retardant in the mean of smoke suppression and thermal stability, corrosion inhibitor, preservative[7]. Toxic and corrosive materials are not emitted through combustion reaction by using zinc borate. Thus, zinc borate is preferred as a fire-retardant additive in swelling coatings due to its characteristic[8]. In one research, boron compounds which have various proportions were mixed with styrene acrylic paint. Also flame retardancy, smoke suppressive abilities and antibacterial properties of two different organic coatings were examined[9]. Diatomite reactive silica substance and significant blain value have important effects on mechanical properties as proven in past studies therefore diatomite is used widely as an additive. Lately diatomite used as an additive in cement for enhancing its properties[10]. In coatings which includes epoxide and epoxy ester binders, effect of diatomite and calcined kaolin against mechanical and anticorrosive properties were investigated[11]. Clariant Nuva HPC can be described as a fluorinated-based commercial compound. Fluorinated compounds are diffusedly used in wide range of materials such as, antifouling and self cleaning coatings etc. Thanks to the irremarkable water repellency, low surface energy, well thermal and chemical stability[6]. In recently, there was an increasing attention on studies of superhydrophobic surfaces, due to their applications, for instance, self-cleaning and nanofluidic[12]. Design Expert optimization method is a statistical method to improve the quality of products and to decrease cost in engineering applications. In this method, the parameters and their levels are selected. The data is analyzed and the verification experiment is performed[13].

In this study, minerals (clay, boron, etc.), which are widely found in Turkey, are preferred as natural additives. The effects of additives added to the epoxy organic coatings on corrosion, hydrophobicity, adhesion, gloss, covering were investigated. The properties of epoxy coatings with new properties were evaluated by neutral salt spray test, contact angle (CA), surface free energy measurement, scanning electron microscope (SEM), Thermogravimetry/ Differential Thermal Analysis (TG/DTA). According to the obtained results, in epoxy resin organic coatings it was observed that zinc borate enhanced flame-retardant effect, diatomite generated anticorrosive effect and Clariant Nuva HPC, a fluorine-based methacrylate-based surfactant, created a hydrophobicity effect.

Experimental Section

Materials

Zinc borate (A),which is a boron mineral, was supplied by Çolakoğlu A.Ş. in Turkey. Clariant Nuva HPC (B), which is methacrylate-based surfactant and diatomite (C), which is a powdery-non-metallic mineral were provided from DuPont and a mining company, respectively. In addition, epoxy resin organic coating was supplied by Kayalar Kimya Genç Noroo Industrial Coatings in Turkey.

Methods

In a 200 g epoxy resin solvent-basedcoating which diluted with some synthetic thinner, 0-6% by mass (w/w) of materials having different properties were added. The additives were homogenized by using mechanical stirrer. The coating was stirred at 1000 rpm for 5 min. The applicator film thickness was 60 μm. The amount of additives to be added was determined by using Box-Behnken Optimization Method in the Design Expert program with applying 3 parameters and 3 levels. Diatomite was added to the epoxy resin solvent based organic coating by grinding and crushing.As a result of this process for each set; based on the Box-Behnken method, 15 different organic coating mixtures were prepared with different proportions of additives (Table 1). Before the epoxy resin organic coatings were applied to the metal surface, 1/7 ratio of (1 gram of hardener versus 7 grams of coating) hardener was added.

Viscosity measurement was done with Lamy Rheology brand RM100 viscometer. The sheen values of the coatings applied to the metal sheet plates were read as 20°, 60° and 85° by using Sheen Glossmaster and Haze Gloss brand measuring devices, respectively. The coverage values of the different mixtures of coatings applied to Zebra paper with the help of the applicator were read by the X-Rite spectrophotometer. In addition, hydrophobicity, corrosion and adhesion tests were performed to surfaces.

Results and Discussion

Design expert results

Design Expert Version 7.0.0 (State-Ease Inc., Minneapolis, MN, USA) was used for the design of the experiment, regression analysis, statistical analysis, response surface graphs and optimization. As seen in the variance analysis table for the viscosity value of epoxy resin organic coatings, the p value of the model was calculated as 0.0429 and it was determined that at least one of the independent variables had a statistically significant effect on viscosity ($p<0.05$). Only quadratic effects of the parameters were found to be significant on the response ($p<0.05$). Of these parameters, zinc borate (A-A), diatomite (C-C), Clariant Nuva HPC-Diatomite (BC) and Clariant Nuva HPC-Clariant Nuva HPC (B^2) additives have been observed to have

Table 1 — Three factor three level Box-Behnken design

Experiment No.	X_1	X_2	X_3
1	-1	-1	0
2	-1	+1	0
3	+1	- 1	0
4	+1	+1	0
5	-1	0	-1
6	-1	0	+1
7	+1	0	-1
8	+1	0	+1
9	0	-1	-1
10	0	-1	+1
11	0	+1	-1
12	0	+1	+1
13	0	0	0
14	0	0	0
15	0	0	0

Table 2 — Variance analysis findings related to viscosity value

Variation source	Sum of squares	Average square	F-value	p-value
model	6.839E+005	75991.70	5.15	0.0429*
A-A	1.205E+005	1.205E+005	8.17	0.0355*
B-B	12.50	12.50	8.471E-004	0.9779
C-C	1.260E+005	1.260E+005	8.54	0.0329*
AB	5329.00	5329.00	0.36	0.5741
AC	10404.00	10404.00	0.71	0.4394
BC	1.665E+005	1.665E+005	11.28	0.0201*
A^2	6181.56	6181.56	0.42	0.5460
B^2	2.081E+005	2.081E+005	14.10	0.0132*
C^2	29963.10	29963.10	2.03	0.2135
Residual	73779.67	14755.93		
Lack of fit	73771.00	24590.33	5674.69	0.0002
Pure error	8.67	4.33		
Total	7.577E+005			

A: Zinc Borate; B: Clariant Nuva HPC; C: Diatomite* significant ($p < 0.05$)

Table 3 — Statistical parameters for viscosity model compatibility

Model	Std. Deviation	C.V.%	R^2
Quadratic	121.47	8.41	0.9026

Table 4 — The coefficients and the importance of the variables in the regression model for viscosity

Variables	Coefficients
Constant	1544.33
A-A	122.75*
B-B	-1.25
C-C	-125.50*
AB	-36.50
AC	-51.00
BC	204.00*
A^2	-40.92
B^2	-237.42*
C^2	90.08

a significant effect on the viscosity value of mass %. The p value calculated as 0.0002 in the lack of fit test shows that the lack of fit is insignificant. R^2value of the model was found to be 0.9026 and it shows that 90.26% of the variability in experimental data can be explained with this model. In the experiment set, it was determined by using Box-Behnken method that coating number 9 had the optimum properties. The coefficient of variation (C.V.) determined was 8.41%. A low value of C.V is a sign of high reliability and also high precision of the conducted experiment[14]. Adequate precision value which should be higher than 4 was calculated as 8.308. Therefore, this model was found to be sufficient to predict new observations. Table 2 shows the results of the analysis of variance for the viscosity value of epoxy resin coating. In Table 3, statistical parameters for viscosity model compatibility were given. In Table 4, the variables and coefficients in the regression model for viscosity were given (Fig. 1).

The linear regression model determined for viscosity is as follows:

$$\text{Viscosity} = +1544.33 + (122.75 \times A) - (1.25 \times B) - (125.50 \times C) - (36.50 \times A\text{-}B) - (51.00 \times A\text{-}C) + (204.00 \times B\text{-}C) - (40.92 \times A\text{-}A) - (237.42 \times B\text{-}B) + (90.08 \times C\text{-}C)$$

Test results

Reference and epoxy resin organic coating mixtures prepared in different formulations were applied to iron sheet plates. Optimum properties of organic coating mixtures were determined by Box-Behnken optimization method. All organic coating mixtures were subjected to physical and chemical tests such as adhesion test, hydrophobicity test (contact angle and surface free energy measurement) and Salt Water Mist test. In addition, organic coating mixtures with optimum properties were subjected to characterization analysis (TG/DTA and SEM Analysis).

Adhesion test

The adhesion grade of the organic coatings on the metal surface is obtained according to the TS 4313 with standard adhesion test. In this test, after the organic coating film sprayed onto the iron sheet plates has completed the drying process, horizontal and vertical lines are drawn with the cross cut at right angles. The tape is glued on the surfaces on which these lines are drawn so that no air remains between the tape and the plate. One end of the tape is released and pulled perpendicularly to the surface in a sudden movement.

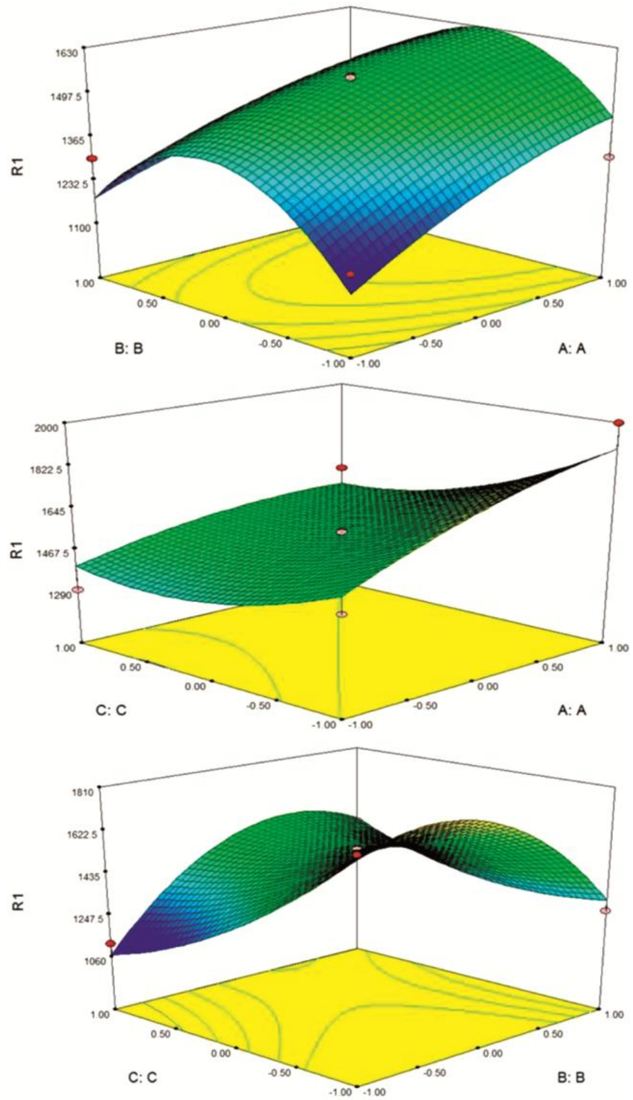

Fig. 1 — 3D Response surface graphs for viscosity

When adhesion test was applied to organic coating mixtures having optimum and reference properties of epoxy resin organic coatings, no spillage was observed in the squares formed by scanning and in the corners of these frames. The additives added to the reference organic coatings did not cause any deterioration on the surface of the organic coating film and did not have an effect to reduce the adhesion resistance.

Hydrophobicity test

In this study, the water absorption behavior of the organic coating samples with (0%, 1.5% and 3%) and without additives were investigated. To determine the hydrophobic or hydrophilic structure of the coating surface, the coating surface is wetted with a drop of deionized water from a syringe. The plates were slowly brought upright and the flow of water on the plate surface and the wettability left on the plate surface were examined. One way to measure the surface wetting properties of a liquid on a coating surface is to measure the contact angle of a drop of liquid placed on the coating surface. The contact angle is the angle formed by the coating-liquid interface with the liquid-vapor interface and measured from the side of the liquid. It is known that solid surfaces indicate the degree of hydrophobicity or the degree of wetting ability. In order to investigate the hydrophobicity more accurately, the angle of the droplet with the paint surface was measured with the Krüss Mobile Surface Analyzer Brand Contact Angle Measuring Device. The sharpness of the drop was adjusted via the mechanical part on the contact angle device and the camera. The drop was photographed and the contact angle was measured by opening the photograph in the Krüss Advance program. Three measurements were made for all coating samples and the values were placed in the tables by taking the average of these measurements. Surface free energies were calculated by entering the measured contact angle values of the samples into the Krüss Advance program using the surface tension method. The contact angle obtained was used in the comparative analysis and thus the coating surface was characterized. The higher the contact angle, the higher the hydrophobicity of the coating. Surface free energy in organic coatings and surface treatment processes must be calculated. With this value how the coating surface will interact with the liquid in contact can be predicted. The contact angle values and surface free energy (Mn/m) values of the plates coated with epoxy resin coatings are given in Table 5. When the values are examined, it is observed that the surface free energy decreases as the contact

Table 5 — Contact angle values and surface free energy values of the plates

No	Contact angle (^{o})	Surface free energy (mN/m)
1	96.44	25.23
2	95.58	25.76
3	101.95	21.86
4	93.26	27.20
5	97.39	24.64
6	93.01	27.35
7	95.40	25.87
8	98.41	24.02
9	87.54	30.76
10	86.27	31.55
11	97.25	24.73
12	90.21	29.10
13	83.76	33.12
14	91.60	28.23
15	96.92	25.15
Ref.	81.74	34.39

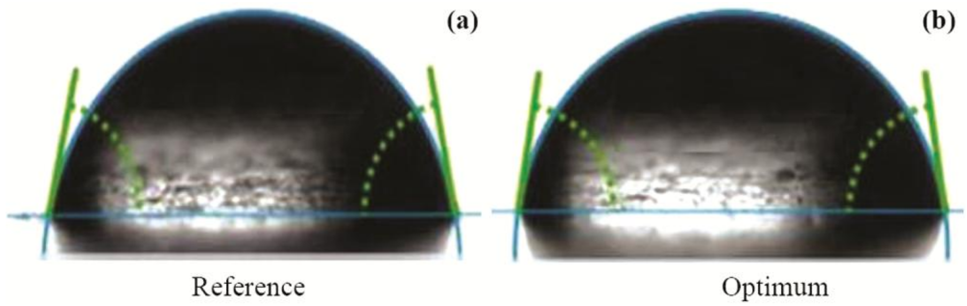

Fig. 2 — Contact angle images of organic coatings: (a)- Reference (b)- Optimum

angle value increases. The contact angle of the drop from the right and left of the surface with the surface was measured as shown in Fig. 2.

The measured contact angle of the reference organic coating is 81.74°. The contact angle of the coating with the determined optimum properties is 87.54°. When the contact angle values are considered, it is seen that the optimum organic coating has a higher contact angle value than the reference organic coating which indicates higher hydrophobic properties. Thus, it has been found that the additives added to the organic coating have a positive effect on the hydrophobicity values (Table 5).

Salt spray test

ASTM B117 salt spray test is the most widely used booth test to evaluate the corrosive performance of organic coatings in an accelerated corrosive environment. ASTM B117 states that the test is useful to provide relative corrosion resistance information for samples in a given test room, but the prediction of performance in natural environments is rarely associated with salt spray results. According to ASTM B117, the amount of corrosion observed is highly dependent on the type of materials tested and the control of operating variables (eg, atomization, salinity, temperature). In this study, corrosion performance tests were conducted to investigate the effect of additives on the product and to compare the corrosion resistance of the resin types. This test was carried out in the salt spray room of Kayalar Kimya Genç Noroo Industrial Coatings. After the plates to be tested are prepared, they are placed in a closed cabinet in which a neutral salt solution of 5% is sprayed at a temperature of 35 ± 2°C according to ASTM B117. The plates to be tested were scratched with a sharp tool to reveal the underlying metal before the corrosion test. The plates are placed in the cabinet at a 15-30° right angle, preferably parallel to the fog flow in the chamber.The plates should be placed in the cabinet so that they do not prevent each other from being exposed to salt water spray. The plates were sprayed with 5% Sodium Chloride at 0.7-1.4 bar air pressure. The 5% neutral salt water that makes up the fog in the cabin was prepared using NaCl and ultra-pure water (conductivity <0.1 µS/cm) at each time of analytical purity. Corrosive mist creates 100% relative humidity inside the room. The exposure time of the test sample to corrosive fog varies depending on the type and thickness of the coating. In the test cabinet, a volumetric tomb with a funnel was placed and the salt water pressure was determined, providing an average salt water accumulation of between 1-2 mL per hour, and this pressure value was used in all tests. Thus, the fog density applied to all samples is homogenized and a standard corrosive environment is provided. Since the spray is continuous, the samples are constantly wet and therefore subjected to constant corrosion. The Salt Spray Test was applied to all samples for 96 hours. Visual inspection of the organic coating film was performed at 24-hour intervals. Due to the higher hydrophobicity and water-repellent properties of the surface, less bubbles are seen on the surface and around the coating than the reference material after the addition of additives. Corrosion on the coating surface after 96 hours is very low compared to the reference material. Thus, it can be concluded that the corrosion resistance of organic coating mixtures increases as a result of the addition of additives (Fig. 3).

Characterization Tests

TG/DTA analysis

In order to determine thermo-oxidative stability of reference and optimum coating mixtures and to investigate the effects of temperature-dependent reactions on mass loss; in the system where nitrogen gas was passed, the mass change of the coatings starting from 30°C up to 810°C with an increase rate of 10 °C/min was examined. TG/DTA analysis results of coating mixtures with reference and optimum properties are shown in Fig. 4 and Fig. 5, respectively.

Decomposition temperatures of additives changed between 250-600°C [15-17]. It is seen that the mass loss of 2.2% up to 245°C is due to the evaporation of the solvent mixed with the organic coating. The main structural degradation occurred in the temperature range of 245-510°C, where 27.584% of material loss was observed. In the temperature range 510-808.6°C mass loss of 8.031% was observed. An endothermic curve occurred in the temperature range 298-500°C. The decomposition temperature of the reference organic coating is 381.15°C. Zinc Borate, Clariant Nuva HPC and diatomite additives prepared with the organic coating mixture; it can be said that the decomposition temperature starts at higher temperature values (392.75°C) compared to the reference organic coating. Accordingly, it can be interpreted that the additives added to the paint impart flame retardant properties.

Fig. 3 —Images after 96 hours of reference and optimum plates

Organic coating with optimum properties; 0.916% up to 150°C; 1.619% between 150-295°C; 25.307% between 295-510°C; 1.916% between 510-585°C; 5.870% mass loss between 585-808°C is observed. The endothermic curve has been formed in the temperature range of 300-500°C. The decomposition temperature of the organic coating with optimum properties is 392.75°C.

SEM analysis

Scanning Electron Microscopy (SEM) (Zeiss EVO® LS 10) was used to examine the physical morphology of organic coating materials.The specimens were magnified 100,000 times and the surface structures were examined and the differences evaluated[18]. The SEM image obtained by spraying the reference and optimum organic coatings on iron sheet plates and is given in Fig. 6. SEM analysis results

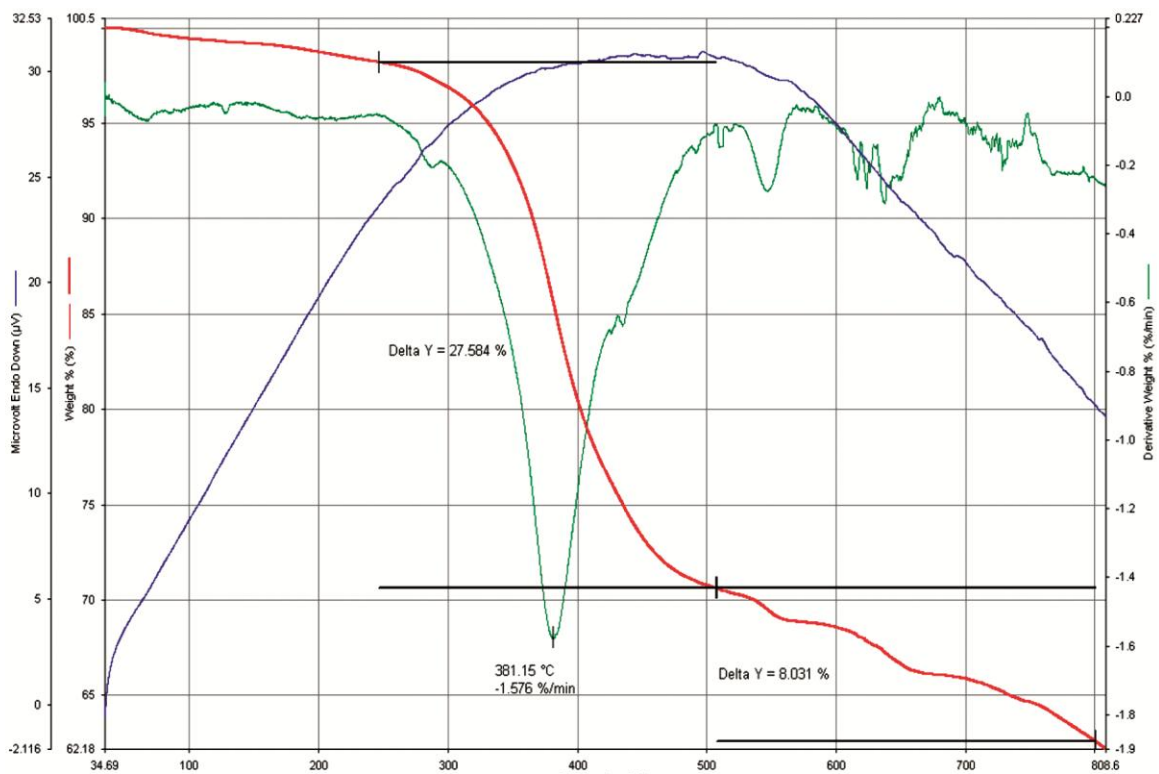

Fig. 4 — TG / DTA analysis of reference organic coating

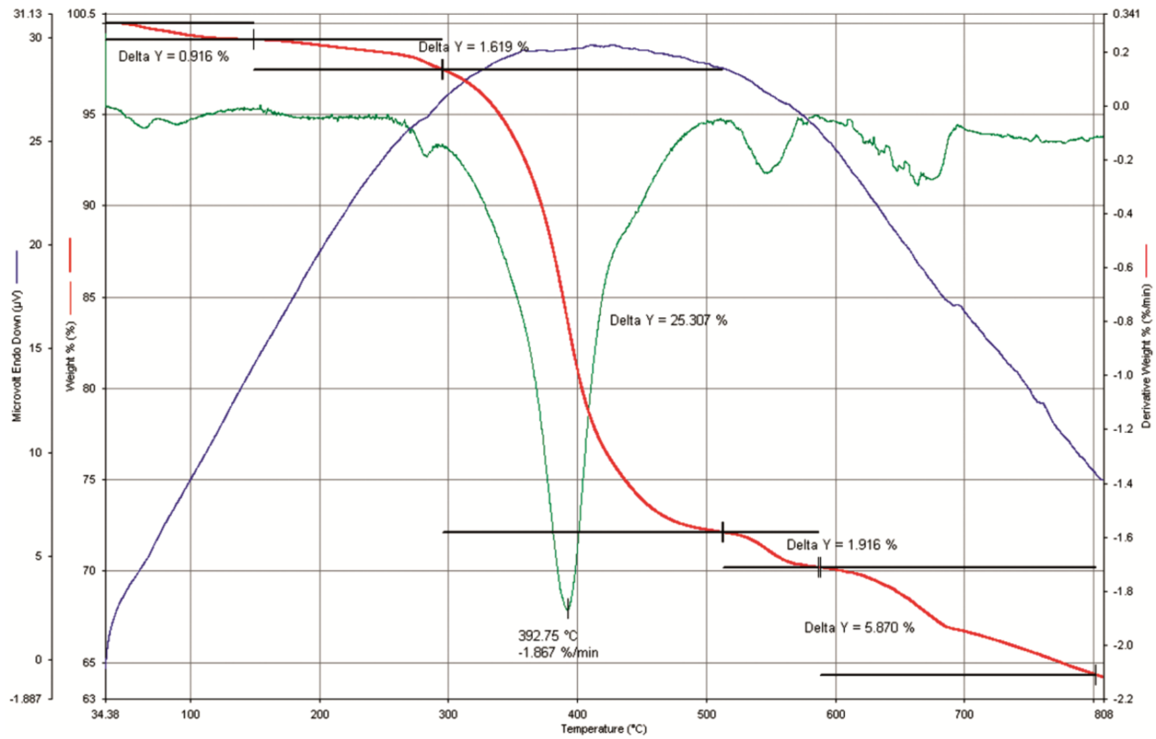

Fig. 5 — TG / DTA analysis of optimum organic coating

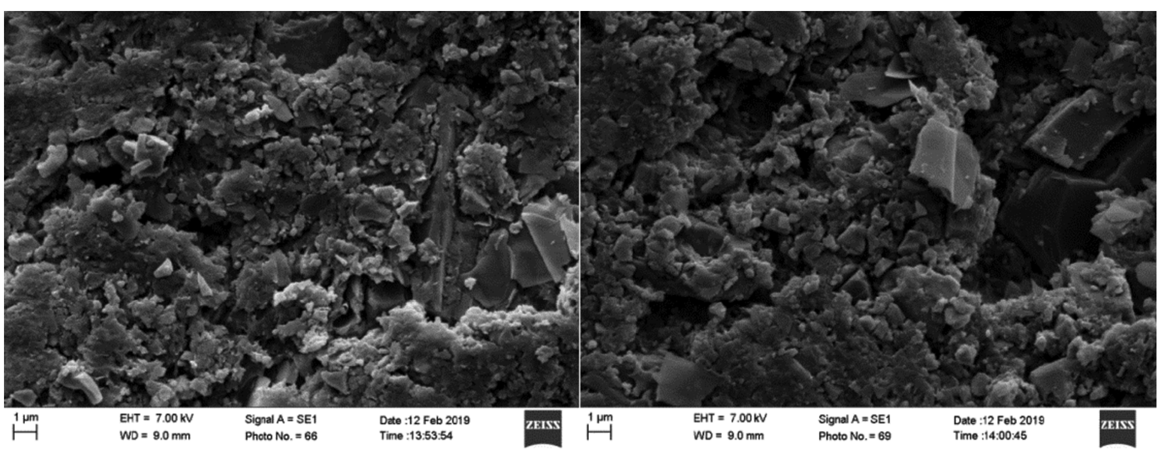

Fig. 6 — SEM images of the reference and optimum organic coatings

were the strong fragmentation of the chemical species in a micro area, whereas the size of the material particles is smaller than the beam current diameter and interaction volumes[19]. The literature showed that fluoro-based surfactant could be increase the adhesion of coating[20]. When the reference and the SEM images of the optimum coating were compared, it was seen that more homogeneous, smooth structures were formed in the optimum organic coating mixture. The particle sizes for the reference coating mixtures are about 278-1388 nm. For the optimum organic coating mixture, it ranges from 223-593 nm.

Conclusion

In this study, corrosion protection performance of the coatings has been improved, in addition, self-cleaning (hydrophobicity) properties and flame-retardant properties have been improved with additives added to epoxy resin coatings in different ratios[21]. By changing the optimization methods, using different additives (different minerals to provide corrosion resistance, different methacrylate based surfactants for hydrophobicity, different boron additives to improve flame retardant properties) and using coatings containing different types of resins (alkyd resins, polyester resins, polyurethane resins, amino resins, polyvinyl chloride (PVC), acrylic resins, silicone resins) the properties of the coatings can be further improved and the resulting new coating mixtures can find various uses in the metal industry.

Anti-corrosion properties and mechanical effectiveness of the achieved new coatings that contains various types of additives were investigated. The results showed clearly that the pure epoxy coating exhibited corrosion protection activity but when combined with diatomite it formed adherent and uniform coating layer that exhibited much higher corrosion protection. In conclusion, the incorporation of diatomite with the epoxy coatings which contains additives are promising for future anti-corrosion applications and should be further studied in the long-term with using additives that contains different properties.

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