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AUTONOMOUS SELF-HEALING COATING OF PMMA MICROCAPSULES FILLED WITH EPOXY

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Abstract

Composites that owns healing property has acquired wide range of application especially in coatings. Microcapsules embedded coatings provide both damage protection and damage management imposing itself among the sophisticated applications. Although the microcapsules coatings have spectacular aspect, their effect on coating properties still under study due the broad properties variation of microcapsules. In this work, PMMA microcapsules filled with Bisphenol-A epoxy is incorporated into epoxy coating. The coating is self-healing and can be used for anti-corrosion applications. The properties of the prepared coating were investigated via scratch test and through microhardness test and the healing process is monitored through optical microscope. The investigation shows that embedding microcapsules into epoxy matrix will achieve both in self-healing coating and better performance.

Keywords: microcapsules, scratch hardness, anti-corrosion, self-healing

1. INTRODUCTION

Self-healing materials attracted many attentions in the past few years due to their enhancements in service-life of materials by providing protection and protective response against visible and hidden damages (1). One particular type of prevalent approaches for producing self-healing coating is microcapsules-based materials (2). Coatings that are based on microcapsules initiate healing process when cracks presents as a result of damages, then the liquid healing agent stored it the microcapsules is released into the crack to fill it and solidify by different chemistries and mechanisms creating protective layer (3). The first coatings based on microcapsules approach was presented by White et.al in 2001. The system is based on ring-opening metathesis polymerization between Dicyclopentadiene and Grubbs' catalyst (4). The following years the research in this field expanded and different healing chemistries and mechanisms were developed, such as healing agent cross-linking with oxygen (5), reacting with sunlight (5) and moisture (6). Moreover different types of healing agents have been encapsulated and employed for self-healing purposes such as Epoxy and hardener (7), amines (8), isocyanates (9), corrosion inhibitors (10) and organic siloxanes (11). In addition to the mentioned above, the microcapsule itself undergoes many changes such as double walls (12) and multi core (13). Although there is increasing development in this field, studies in terms of mechanical properties for microcapsules-containing coating and micromechanical properties of the microcapsules still insufficient, for instance Ahangaran et.al studied the micromechanical properties of PMMA microcapsules filled epoxy (EC 157) and mercaptan be means of nanoindentation (14). Liang et.al managed to develop composite coating that not only is able to mend itself but also it has scratch resistance through incorporation of modified silica nanoparticles (15). Wang et.al introduced failure analysis for self-healing anti-corrosion epoxy coatings filled with Linseed oil containing poly-ureaformaldehyde microcapsules stating that the system is successful in terms of producing self-healing property but when immersed in 3% NaCl it will deteriorate immediately (16). In this work pre-prepared microcapsules of Bisphenol-A based epoxy and amine-based hardener will be integrated in Bisphenol-A epoxy matrix. The system is investigated for its self-healing capability and validity for coating applications.

2. MATERIALS

Both Epoxy (Bisphenol A-based) and hardener (Amine-bases) were purchased for Sika Co. Ltd

under trade name Sikadur 52 LP. Poly methyl methacrylate (PMMA) is chosen as shell material. Dichloromethane (DCM) from central drug house India is chosen as solvent. Sodium dodecyl sulfate (SDS) from HI Media Laboratories, India is chosen as surfactant.

3. EXPERIMENTAL PROCEDURES

3.1. Preparation of PMMA-shell resin & hardener core microcapsules

Approach adapted for preparing PMMA-microcapsules filled with Epoxy and hardener is solvent evaporating. At first the microcapsule component (Epoxy & PMMA) dissolved in 30 ml of DCM with 1 g of each component. Pre-made aqueous solution of 3% SDS was prepared, after microcapsule component dissolved, it was added to the 50 ml pre-made aqueous solution of SDS with stirring for half an hour, the transfer the mixture into 200 ml aqueous solution with the same concentration. The temperature at this point was raised to about DCM boiling point, after evaporating of DCM the solution was filtered and dried. Schematic representation of the process shown in Figure (1).

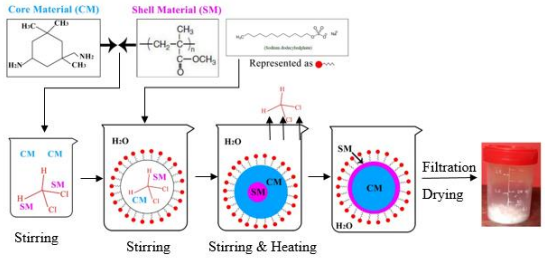

Fig. 1. Schematic represent for the encapsulation via solvent evaporating

3.2. Preparation of self-healing coating

In order to prepare self-healing specimen, a steel substrate were coated by epoxy and epoxy-microcapsules with different portions. Doctor blade coating technique employed for this purpose, the specimen is cover with tape as the required thickness on the sides and then coating is poured on the surface and drawn with blade as shown in Figure (2). The stoichiometry for epoxy resin with hardener is (2:1) and for microcapsules (1:1). Four specimen were fabricated, pure epoxy coating and epoxy coating with (10, 15, and 20) % wt. microcapsules coating to be observed by optical microscope and two specimen were fabricated to check the validity of the self-healing in coating applications.

3.3. Characterization

FTIR test was executed using (IR Affinity-1). Scratch test was carried out on a Scratch Machine (Surface Machine Systems, China) as according to the ASTM D7027-05 and ISO 19252:08 standards. Scratch hardness was determined using the following formula (17):

$$Hs = \frac{q4w}{\pi d^2} \quad (1)$$

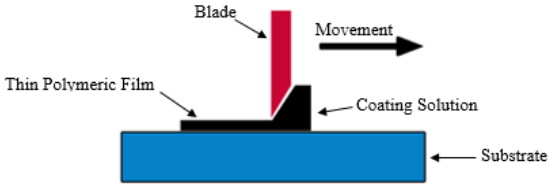

Fig. 2. Doctor Blade technique for producing thin coatings

Where: (Hs) is scratch hardness (MPa), (w) applied force (N), (d) groove width (mm), (q) parameter between 1 and 2 due to viscoelastic and viscoplastic behavior, for polymers is equal to 1.5. In order to investigate the micro hardness of the coated samples, Vickers microhardness test was carried out. Microhardness was determined using the following formula (18):

$$Hv = \frac{KP}{L^2} \quad (2)$$

Where: (K) constant valued 1.854, (P) the applied load (N) and (L) average diagonal length (mm). The test was carried out for all specimen (0, 10, 15 and 20) % capsule content. In order to investigate the success of the healing process, Optical microscope is employed. Optical microscope employed to assess the healing process according to ASTM F728-81 standards and also simple corrosion test was conduct to assess the healing ability. FESEM was conducted to investigate morphological and size properties of the microcapsules. The information gathered of FESEM analyzed using image processing software. The device used is (MIRA3 TESCAN). TGA properties were conducted with SDT Q600 TA Instruments.

4. RESULTS & DISCUSSION

4.1. FESEM analysis

As shown if Figures (3) & (4), the majority of microcapsules have spherical shape and no abnormal shapes are observed. In addition to the uniform shape and smooth surface features which will eventually promote uniform distribution. Microcapsules sizes between the epoxy and hardener are similar as shown in Figure (5) with average diameter of 8.9 μm for the epoxy-based microcapsules and 7.1 μm for hardener, this narrow deviation between resin and hardener microcapsule size will promote random rupture and the release of similar component quantity of the resin and hardener leading to higher reaction rates. The surface free porosity indicates that evaporating temperature is near or below the boiling point of DCM is favored.

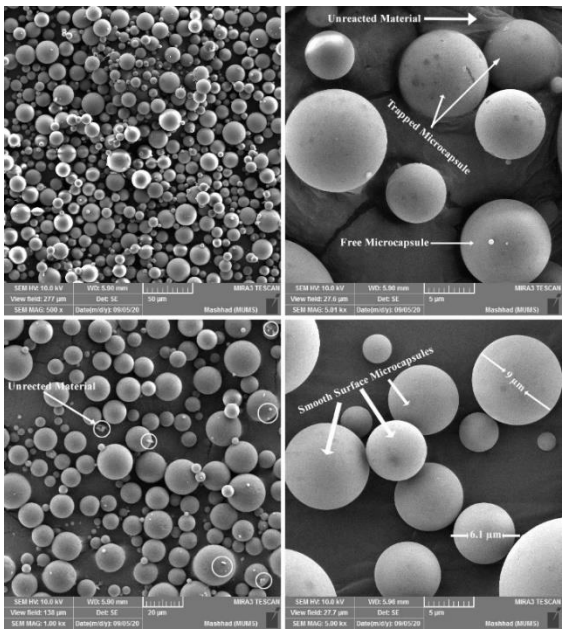

Fig. 3. FESEM for PMMA microcapsules filled with epoxy resin

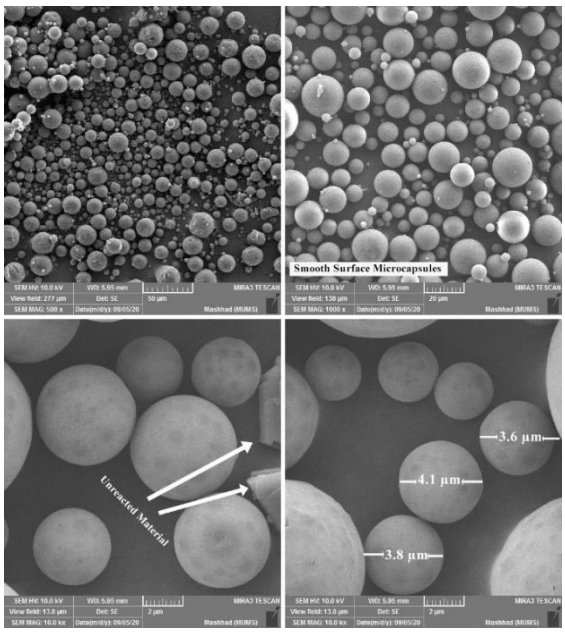

Fig. 4. FESEM for PMMA microcapsules filled with amine hardener

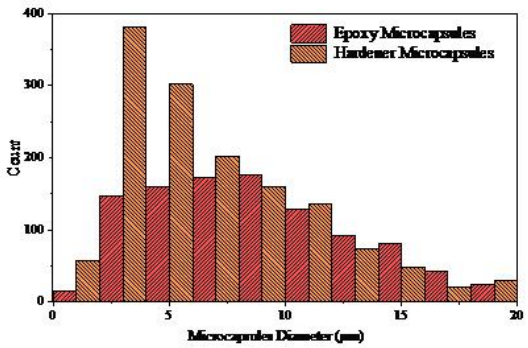

Fig. 5. Size distribution of microcapsules

4.2. FTIR analysis

The successful encapsulation process is proven by FTIR test. The obtained results for both PMMA filled with epoxy and hardener microcapsules with their raw substance are shown in Figures (6a) (6b). The obtained results confirming that encapsulation has done successfully and in Table (1) the functional groups can be seen with their assigned wavelength and compared to another sources.

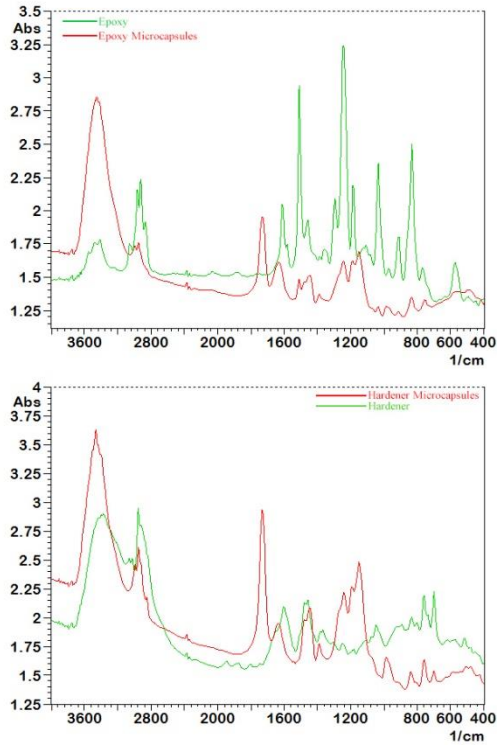

Fig. 6. FTIR for (a) epoxy resin and epoxy-microcapsules (b) hardener and hardener-microcapsule

Table 1. Epoxy peaks compared to other references groups.

Assignments	Wave Number (Cm^{-1})	Ref (19)	Ref (20)	Ref (21)	Ref (22)
C-O-C	1242	1249	1245	1245	1247
Epoxide	910,970	915	910	914,970	915
Aromatic C-O stretching	1033	-	-	1033	1035
Aliphatic C-O stretching	1184	-	-	1184	-
C-C stretching	1512	-	-	1508	-

Table 2. Hardener peaks compared to other references groups.

Assignments	Wave Number (Cm^{-1})	Ref **(8)**	Ref **(19)**	Ref **(20)**	Ref **(23)**
N-H bending	840 & 1635	842 & 1632	830 & 1592	840 & 1571	1650
N-H stretching	3410	3432	3370	3370	3300

4.3. TGA analysis

Because the microcapsules are subjected to heat during composite production, the thermal characteristics of the prepared microcapsules are critical for determining their stability. TGA is a fascinating technique for such purpose. As shown in Fig (7) TGA and DTG curves suggesting That PMMA microcapsules containing resin have two stage degradation starting at 170 °C to 470 °C and the second is above 470 °C. The first is related to shell and core degradation together while the second is for shell only. Hardener containing microcapsules have two stages degradation also the first (200-330) °C which is associated for the amine core material, the second is at (330-460) °C which is related to the PMMA shell material.

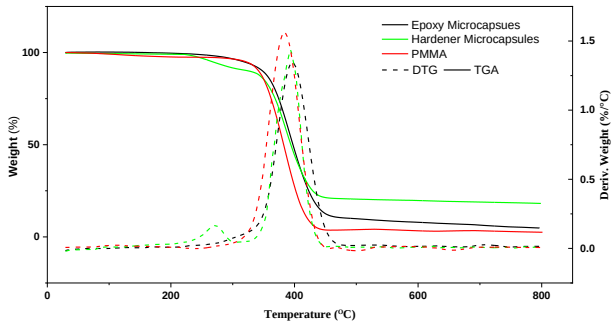

Fig. 7. TGA and DTG for epoxy microcapsules, hardener microcapsules and pristine PMMA

4.4. Self-healing Activity Assess

As it can be seen in Figure (8) (a) and (b) for the specimen with highest microcapsule content (20 wt%), the cut is obviously visible in terms of width and depth, but in Figure (8) (c) and (d) and after 72 hours the difference is found to be obvious, the width and the depth of the crack seems to be changed although the OM technique did not allow us to determine the exact difference in numbers but the images clearly shows decreasing in the crack area width and depth wise. And it is necessary to say that the crack will not be fully closed by using this kind of healing system because a portion of the bulk material is already gone in the cutting process, and the changing here is due to releasing healing agents stored in the embedded capsules and amount of liquid release and reacting efficiency determine the change. In addition, if the crack of control specimen shown in Figure (9 a) is compared with the all the rest, noticeable difference will be observed. The crack at specimen with 10 wt% Figure (9 b) and 15 wt% Figure (9 c) microcapsules shows very slight degree of decreasing crack width, as for crack depth it cannot be taken in consideration with this test. The specimen of 20 wt.% microcapsules seen in Figure (9 d) shows clearly healing and crack closure to satisfactory point. This indicates that more capsule content should be incorporated in order to get acceptable healing process.

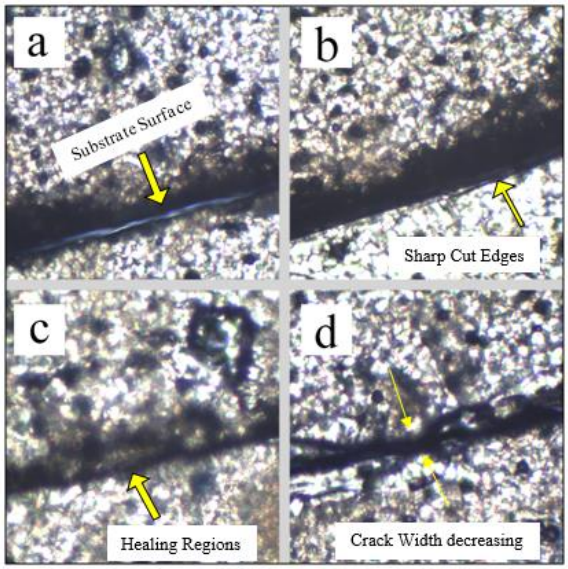

Fig. 8. Optical microscope images for (a) (b) 20 wt.% microcapsules with crack (c) (d) the same specimen after 72 hours

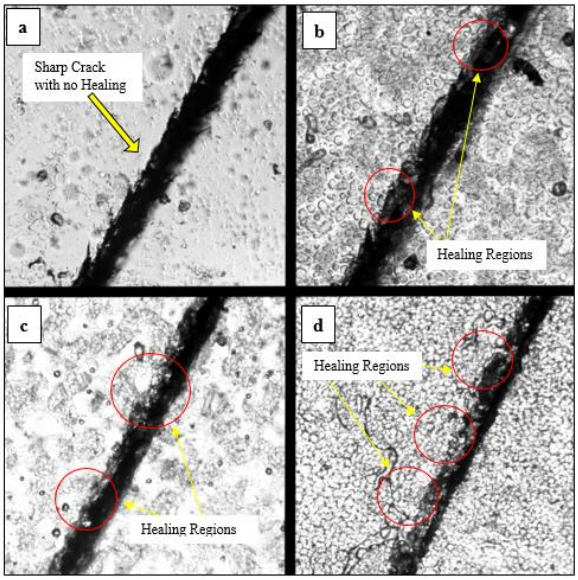

Fig. 9. Optical microscope images for (a) pure epoxy and healed epoxy specimen after 72 hours with (b) 10 wt.% (c) 15 wt.% (d) 20 wt.% microcapsules all at 100X magnification

4.5. Anti-corrosion Self-healing Coating Results

As shown in Figure (10), after scratches were made and the two specimens (pure and 20 wt.% microcapsules) were immersed in 10% NaCl for 48 hours then taken off and left to dry. In case of pure specimen it can be clearly seen that corrosion take place along the crack path suggesting that the electrolyte solution has reach the substrate and initiated corrosion. On the other hand the 20 wt.% specimen shows enormous difference in terms of corrosion spreading, this is due to the layer barrier that formed at crack as a result from the reaction between the two liquid substance stored in the microcapsules during crack occurrence. This result show successful self-healing process.

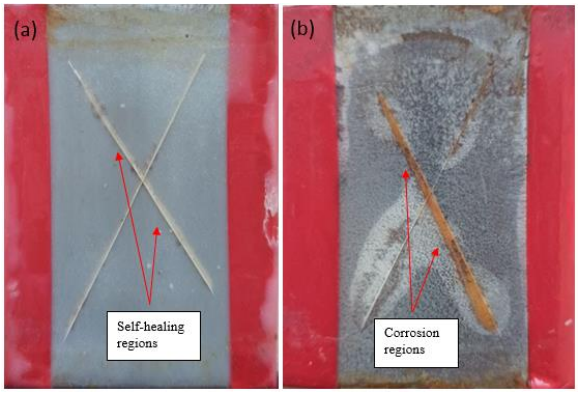

Fig. 10. Corrosion test for (a) self-healing coating sepecimen containing 20% wt. microcapsules (b) pure epoxy coating

4.6. Scratch hardness analysis

Scratch test gives information about scratch hardness which can be considered as indicator for coating cohesion. All the samples were coated with microcapsules embedded epoxy. All the samples undergo specific load in the order of 1, 3, 5 and 7 N for distance of 10 mm for each sample. As it can be seen in Figure (11) and Figure (12), the scratch hardness of pure epoxy coating is 66 MPa. This value increases sufficiently at 10% microcapsules content within the epoxy matrix up to 79.57, the furthermore addition of capsules content to 15% produces scratch hardness at 197.86 MPa. Then at 20% microcapsules content the value decreases to 159 MPa. As it can be seen at 15% microcapsules content the coating has the best value of scratch hardness due to increased interfaces bonding the between microcapsules and the epoxy matrix, this will lead to increase the matrix resistance to deformation causing groove width to decrease and hence better cohesion of the coating. The addition of microcapsules hence will improve the cohesion of the epoxy coatings with the addition to self-healing phenomena.

4.7. Vickers microhardness analysis

As it can be seen from both Table (3) and Figure (13) the hardness for pure epoxy coating is 3.02 with keeping test parameters the same for all specimens. The hardness will increase upon the addition of 10% microcapsules up to 4.19, due to the microcapsules which will act as reinforcement phase within the epoxy matrix and also refers to good and homogenous distribution of the capsule in the matrix. Furthermore addition of capsule content will cause the hardness to drop as it can be seen at 15% capsule content the hardness dropped to 3.93 and at 20% capsule content to 3.54. This decreasing in hardness value is linked to agglomeration of microcapsules since the increasing of the content will lead to bigger possibility of agglomerations to occur within the matrix thus creating weak region and bonding in the matrix leading to decrease mechanical properties. Some researches stated that the smaller the capsules size (<10 μm) the better mechanical performances for the matrix, but further information is needed in terms of the mechanical properties of the microcapsules itself.

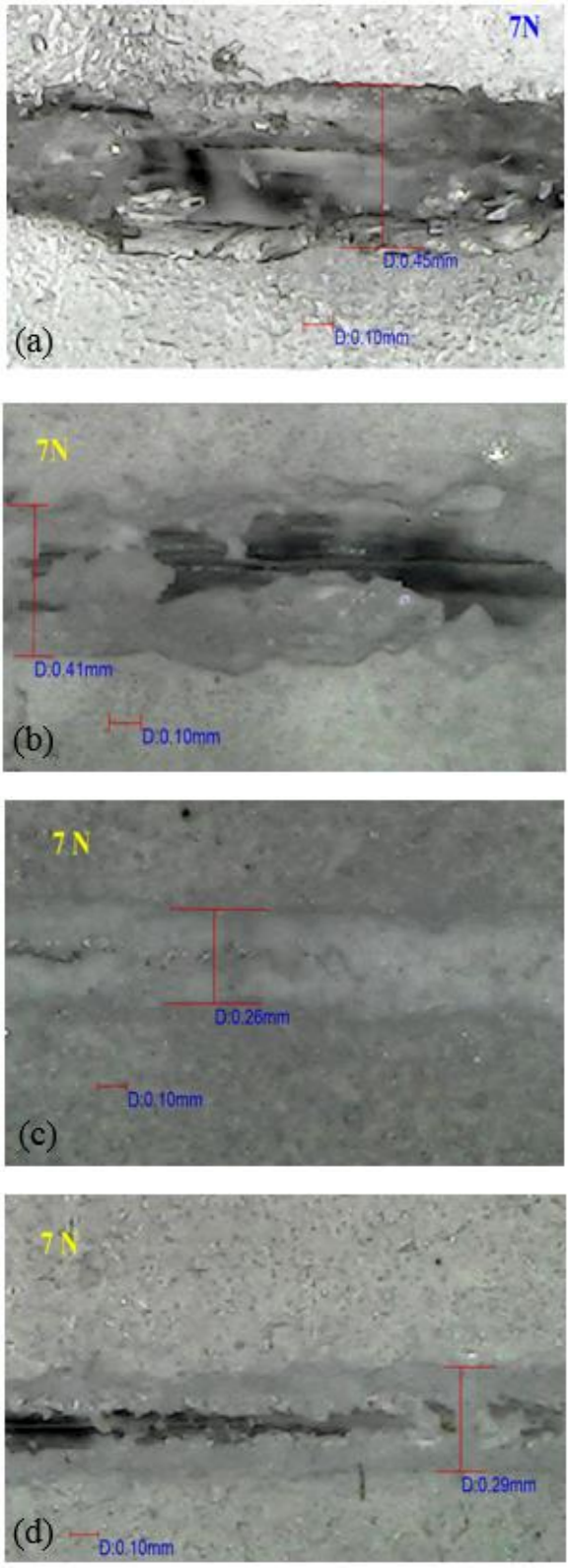

Fig. 11. Optical images for the groove for (a) pure coating (b)10 wt.% (c) 15 wt.% and (d) 20 wt.% microcapsules coating

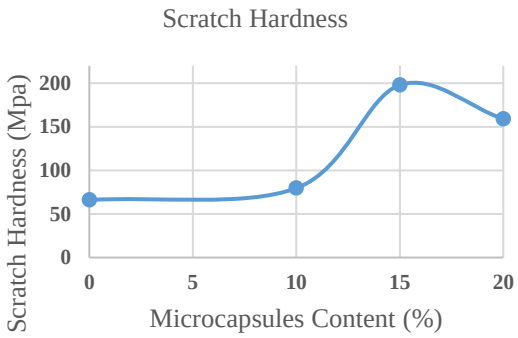

Fig. 12. Scratch hardness curve at different cpasule content

Table (3). Microhardness with test parameters for dual-microcapsules embedded epoxy coating.

No	Microcapsules content (%)	Load (N)	Time (sec)	Hardness
1	0%	0.245	25	3.02
2	10%	0.245	25	4.19
3	15%	0.245	25	3.93
4	20%	0.245	25	3.54

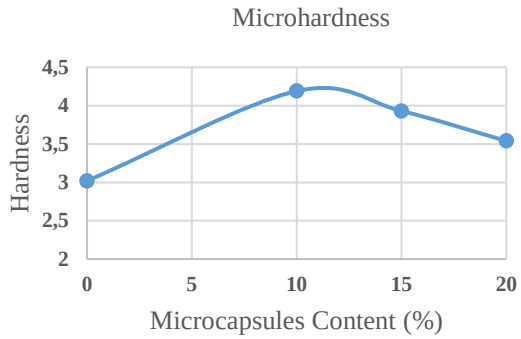

Fig. 13. Microhardness curve for epoxy filled with dual-microcapsules at different microcapsules content

5. CONCLUSIONS

PMMA microcapsules filled with bisphenol-A epoxy and amine hardener successfully incorporated within epoxy matrix with different weight percentages (10, 15, 20) %. The coating is proven to be self-healing as the optical microscopic images suggests, moreover when conducting corrosion test the microcapsules coated specimen offers better anti-corrosion performance than the virgin coating and this along with the optical images prove the self-healing ability. The scratch test for all the specimen shows that specimen with 15% microcapsules have the best scratch hardness value while the lowest was the virgin specimen indicating that the addition of microcapsules at all percentages produce better scratch hardness for the coating. The microhardness results shows that the 10% microcapsule specimen owns the best value. Form these results it can be stated that the prepared coating is better than the virgin epoxy coating besides offering self-healing activity.

Author contributions: *research concept and design, A.F.M.; Collection and/or assembly of data, A.F.M.; Data analysis and interpretation, A.F.M.; Writing the article, A.F.M.; Critical revision of the article, A.F.M., A.F.H., A.E.Al-K.; Final approval of the article, A.F.M., A.F.H., A.E.Al-K.*

Declaration of competing interest: *The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.*

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