Epoxy Based Self-Healing Materials Loaded with Natural Drying Oil: a Future Prospectives

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EPOXY BASED SELF-HEALING MATERIALS LOADED WITH NATURAL DRYING OIL: A FUTURE PROSPECTIVES

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Abstract: During the most recent couple of years, various types of epoxy based microcapsule loaded with natural drying oil self-healing materials have been prepared utilizing assorted strategies for various applications. The consolidation of reasonable functionalities into these materials encourages a healing component that is set off by damage or rupture just as different chemistry. This article presents a investigation of the epoxy based self-healing materials loaded with regular drying oil like linseed oil, tung oil and castor oil. The article will likewise give a review on above natural drying oil utilized in the readiness of epoxy based self-healing polymer composite, alongside their efficiency in healing.

Key words: Self-Healing, Epoxy, Microcapsules, Coating, Corrosion, Drying Oil, Linseed Oil, Tung Oil, Castor Oil

1 Introduction

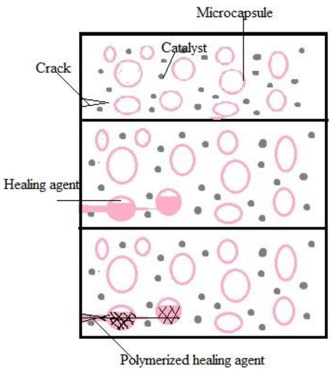
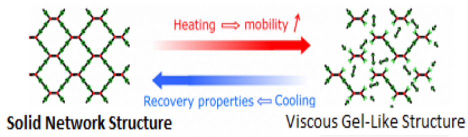
Self-healing materials has gotten extraordinary attraction during the most recent decades since they may altogether add to the expansion in reliability and durability of materials [1]. Similar to living things, self-healing composites have the exceptional capacity to distinguish and healing damages and, therefore, to reestablish their underlying function (completely or partially). Polymer composites regularly experience micro-cracks during their application [2]. The self-healing concept is incorporated where the damage can be healed by the materials already present within the structure. Self-healing polymers have underlying capacity to heal generously their lost load transfer capacity after damage. The ability to self-heal brings about delayed material utility life, less maintenance, and subsequently potential cost decreases [3]. Different sorts of healing material got from nature have been made for microcapsules based self-healing method, epoxy [4], including isocyanates, and different inhibitors. Nonetheless, it is anticipated that the oil based crude materials will short later on because of the worldwide expanding utilization of nonrenewable oil. Simultaneously, biodegradable based materials have pulled in significant consideration in exploration and industry to debilitate the reliance of nonrenewable oil based goods [5]. These days, a noteworthy number of oil based items have been supplanted or adjusted by bio-based crude materials [6]. Among them, a few vegetable oil having drying property is being formed and applied into microcapsules for self-healing coatings or cracks , linseed oil, Tung oil, and castor oil. Prior drying oil utilized with alkyd for coating to shield materials from coating. Be that as it may, the coating by this blend of materials can't give enough erosion assurance. It is needed to build the kind of inexhaustible biodegradable based healing specialists to improve the exhibition of self-healing coatings.

Among all material damages corrosion of metals has been a big problem as reduction of strength of components, which may result sudden failure of structure and heavy economic loss. Thus, to avoid chances of corrosion organic coating has become one of the most common effective methods. However, organic coatings can be subjected to physical damages, such as scratches and cut marks, which may lead to failure of coatings and consequently, water, would penetrate through the coating and lead to the metal corrosion. Hence, self-healing materials have been developed to repair the mechanical damage that appeared on the material by itself, and it can also give quick recovery [7]. The attraction toward self-healing coatings is probably expressed due to their ability to recover damages autonomously after occurrence of any microcracks, which may appear due to excess of internal stress or any mechanical failure. Incorporation of this technique may lead to less maintenance and reduces the chance of heavy economic losses. This is can be used in oil rigs and wind turbines. White et al. have first published article in the field of self healing polymer. The interest to self-healing coatings has increased dramatically after mid 1990 although after White et al. publication in 2001 dramatically increased interest toward the study of microencapsulation method of self-healing materials [8].

The epoxy based microcapsules coatings containing were applied on carbon prepares and their conduct and self-healing impact were examined by numerous scientists. It was discovered that the counterfeit scratches were effectively healed in brief timeframe after made. Nonetheless, coating execution change with increment of epoxy microcapsules among all the readied coatings. Hence, there are numerous techniques for readiness of self-healing materials and generally grouped dependent on various methodologies: Intrinsic self-healing which can heal cracks without anyone else without the guide of any healing specialist, and (ii) Extrinsic self-healing, the healing operator is pre-implanted in the lattice and applied remotely while breaking. To deliver an extrinsic self-healing material, healing operator is contained in microcapsule having capacity to break while any split creates in the materials.

Self-healing process can also be differentiated as automatically and autonomously. Sometime terms such as self-repairing, autonomic-recovery, and autonomic-healing are used instead of self-healing. Self-healing concepts came into mind by natural phenomenon like living things require some external trigger as drugs in the same way self-healing also require external trigger. Thus, self-healing materials can be classified on the basis of intervention [9]. Autonomic and Non autonomic type self healing materials are shown in Table 1

Table 1 Autonomic and Non autonomic type self healing materials

Autonomic	Non autonomic
It can perform without any intervention	It generally requires some sort of outside boost. This boost can be as warmth, light, mechanical or compound upgrade.
	

2 Concept of self-healing techniques based on epoxy resin

In this survey, various kinds of healing cycles are considered as self-healing all in all. Here, self-healing is presented as the materials having attributes to recuperate the mechanical quality through split healing and coating of metallic sheet to keep away from corrosion. In any case, it can used to heal split as well as little pinholes can be healed or filled to have better execution. Consequently, this audit delivers strategies used to recoup various kinds of properties of materials [10]. Epoxy gums have been considered as one of the most significant polymeric frameworks since they can be utilized in a wide scope of utilizations, for example, composites, cements, in coating. It is watched, the microencapsulation of epoxy saps has been pulled in by analysts in light of its boss similarity between the healing operator and the epoxy based polymeric network and recuperate the underlying mechanical properties [11].

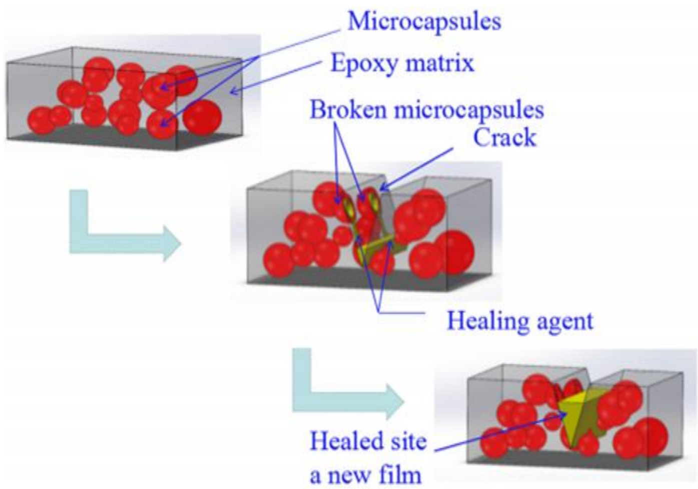


Fig.1- Self-healing mechanism [21].

Self-healing procedure can work just when container burst while split shows up in the material. Accordingly, appropriate mechanical quality of microcapsule has been viewed as the best outside upgrades to deliver the healing operators, which are relied upon to recuperate the harmed surface [12]. Outer mechanical worry of self-healing relies generally upon dynamic healing specialist properties, microcapsule distance across and its shell properties. The self-healing specialist ought to have low consistency to stream effectively into the deformity and ought to be exceptionally responsive to viably heal the harmed. For the most part, it has been viewed as that microcapsule width ought to be in the scope of 50−200 μm, which empower simple crack and guarantee high stacking limit [13].

Materials can be protected against corrosion by several ways [14], generally polymer paints or coatings are used which are among the simplest and the cheapest methods. It can provide satisfactory protection of the material from corrosion [15]. However, while materials get any crack inside or on the surface of material, polymer paints or coating will also subjected to crack and there will be chances of corrosion. Hence, self-healing sort coating is needed to utilize to dodge such sort split. The microcapsule based self-healing method is considered for the investigation of coating execution and break healing effectiveness. These cases stacked with a self-healing specialist are consolidated in the coating. They are burst and delivery the self-healing specialist during split arrangement. There is response happens between the delivered self-healing specialist and an impetus scattered in the polymeric coating which goes through oxidative polymerization and drying, coming about to split fix. Because of polymerization of the delivered healing operator, the cracks are independently fixed. Thusly, these qualities of the compound response of the healing specialist and the similarity between the healing operator and split planes are basic for the level of rebuilding of the materials. Moreover, of response rate likewise decides the pace of recovery. To beat this, quick healing response is has significance so break ought to be dispensed with before the engendering of split. Already, various kinds of technique self-healing, for example, delivering healing operators, transportaion of nanoparticles and cross-joins have been created. White et al. have first time acquainted a method with exemplify dicyclopentadiene as a healing operator in a poly urea-formaldehyde shell of microcapsules [16]. As impetus nearness is an essential part coating framework yet impetus as a subsequent stage results to a ruling heterogeneity in the coating grid [17]. Self-healing materials as a serious polymer coating have been utilized to improve metallic material life against corrosion and reestablish its underlying properties subsequent to splitting because of the outer condition or inner anxieties. Consequently, self-healing coating assists with halting engendering of split and furthermore diminishes collaboration with oxygen, water and ionic materials.

3 Performance of epoxy resin in microcapsule loaded with different natural drying oils

3.1 Healing performance of microcapsules containing linseed oil in cracks

Linseed utilized as a drying oil in coatings, embodied linseed oil in the microcapsule as healing specialist with against corrosion operators was employed to epoxy coatings. The figure portrays the cycle of nanocapsules manufacture, stacking the segments, lastly the properties and execution of the half and half coatings. Nanocapsules preparation and their use in crack healing mechanism is shown in figure 2.

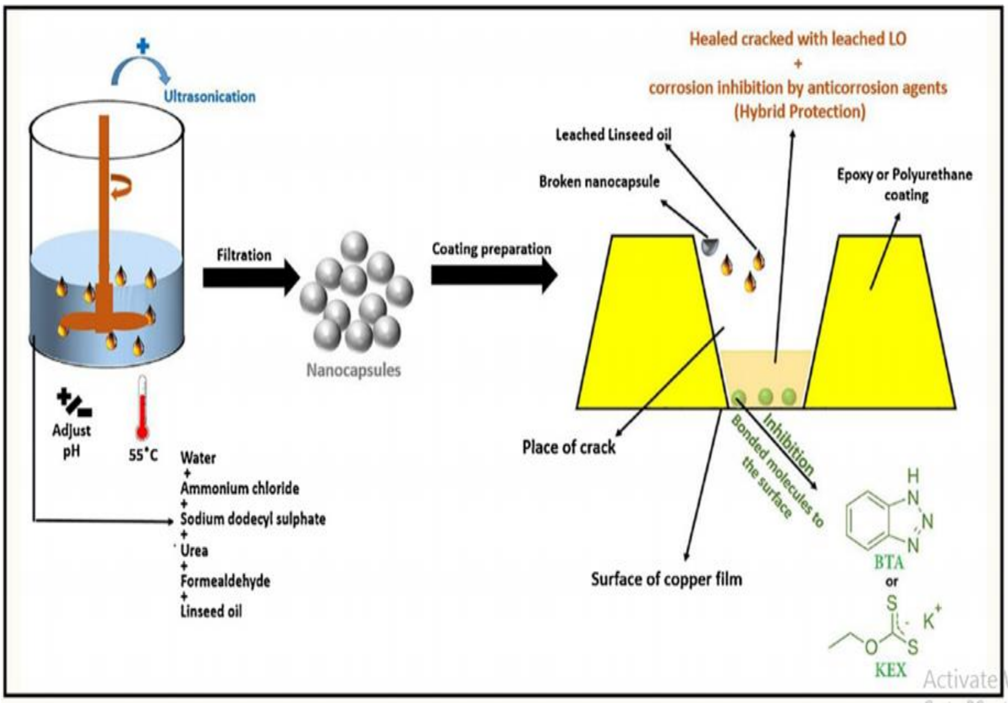


Fig.2- Nanocapsules preparation and their use in crack healing mechanism [18].

It very well may be broke down to test by applying a fake scratch on coating and the sublayer is opened to destructive specialists. Epoxy coatings have a high manufactured and mechanical restriction in this manner can be gone about as a ground-breaking obstacle to the passage of chlorine particles and other ruinous authorities. In any case, linseed oil as self-healing pro in scratched tests is conveyed at hurt domains and fixes the cautious layer. On the other hand, threatening to disintegration masters furthermore can be accepted a key activity in making sure about of tests.Thusly, in light of the advancement of a complex between threatening to disintegration administrator and metal surface, an inert layer is molded.

Surface morphology, thermal stability and size distribution of nanocapsules

It was investigated and analyzed that round shape of nanocapsules have more interface however blunt surface results better interactions between polymer matrix and additives and give an better results for coatings [18]

Further, nanocapsules up to 200 °C were analyzed thermally stable. Furthermore, in thermogram at 200°C and 300°C two mass losses were analyzed, which may be related to linseed oil thermal decomposition temperatures.

Also, size distribution of capsules was investigated between the range of 460 nm to 720 nm diameters. the synthesized nanoparticles had mostly 531 nm diameters of the capsules narrow size distribution. The size of nanocapsule is less than one micrometer thus surface area to volume ratio is more. Hence, interaction with crack sublayer would be more and crack healing time will also be reduced.

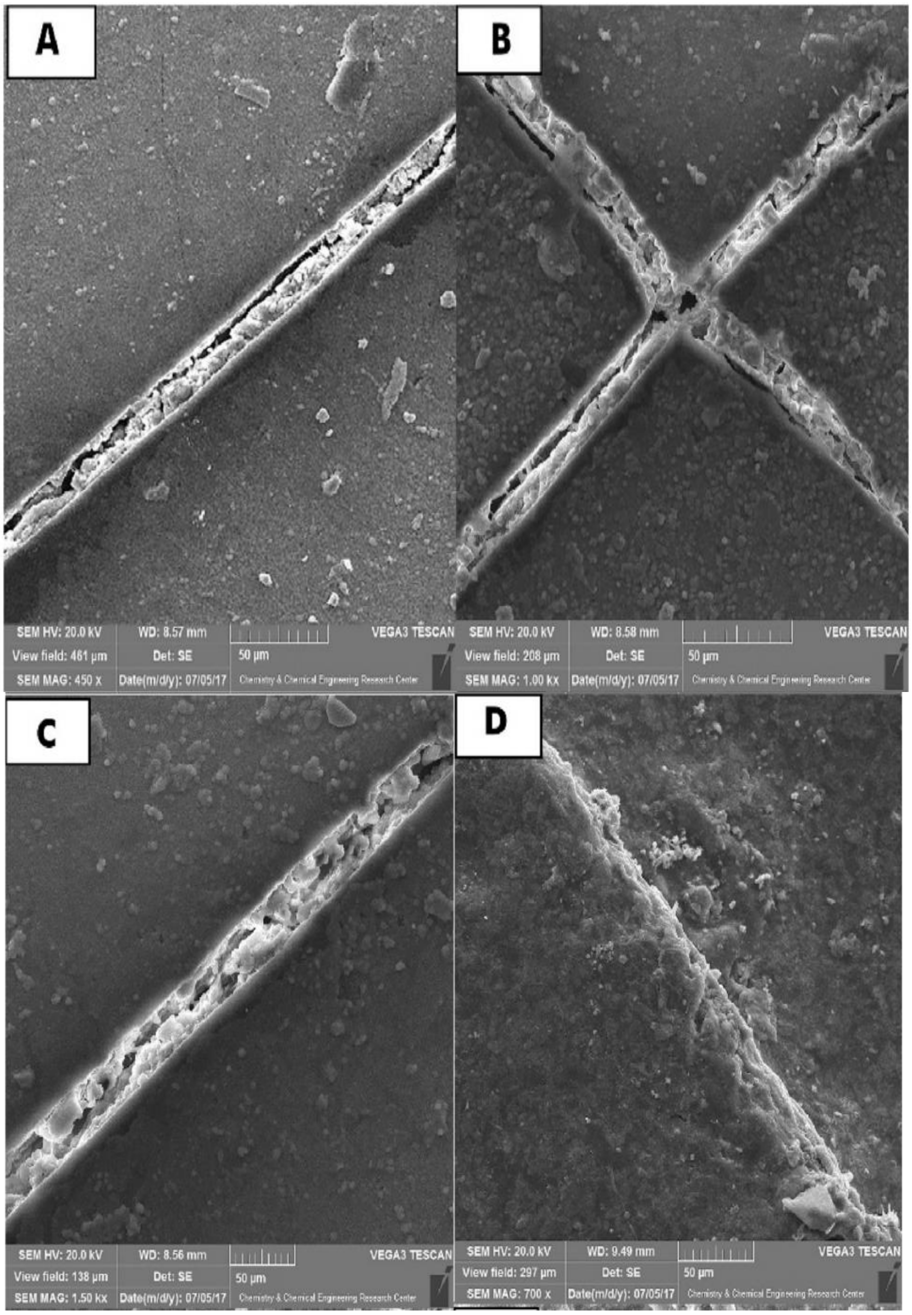
Crack healing capacity

The impact of various parameters on healing cycle was examined in various investigations. In view of the acquired pictures, self-healing cycle happened in practically many coatings which cis having nanocapsules. Table 2 is having the samples which are different type of anticorrosion agent loading.

Table 2 Microcapsules containg anticorrosion agent and type of paint used.

Sample	Microcapsules (wt%)	Anticorrosion agent (wt%)	Type of paint	Type of anticorrosion agent
A	0	0	Epoxy	potassium ethyl xanthate
B	0	3	Epoxy	potassium ethyl xanthate
C	0	5	Polyurethane	benzotriazole
D	3	5	Polyurethane	potassium ethyl xanthate
E	5	3	Polyurethane	potassium ethyl xanthate
F	10	0	Polyurethane	benzotriazole

In itemized overview outlined that sample A have no healing because they didn't have any added substances. Besides, correlation between picture C and D for the duration of 1st day and 7th days proposed that the scratch mark had gotten more filled in contrast with the principal day and it very well may be presumed that self-healing cycle was not halted even subsequent to inundating in corrosive arrangement. Both of the Samples D and F included polyurethane coatings, while the previous is a cross breed coating and the last contained just nanocapsule, it ought to be referenced that both of the samples displayed great healing conduct. Notwithstanding, as it very well may be seen, made scratches were totally loaded up with healing operator as linseed oil in samples D, E and F and it uncovered the healing impact of nanocapsules.


A
SEM HV: 20.0 kV
WD: 8.57 mm
VEGA3 TESCAN
View field: 461 μm
Det: SE
50 μm
SEM MAG: 450 x
Date(m/d/y): 07/05/17
Chemistry & Chemical Engineering Research Center
B
SEM HV: 20.0 kV
WD: 8.58 mm
VEGA3 TESCAN
View field: 208 μm
Det: SE
50 μm
SEM MAG: 1.00 kx
Date(m/d/y): 07/05/17
Chemistry & Chemical Engineering Research Center
C
SEM HV: 20.0 kV
WD: 8.56 mm
VEGA3 TESCAN
View field: 138 μm
Det: SE
50 μm
SEM MAG: 1.50 kx
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Chemistry & Chemical Engineering Research Center
D
SEM HV: 20.0 kV
WD: 9.49 mm
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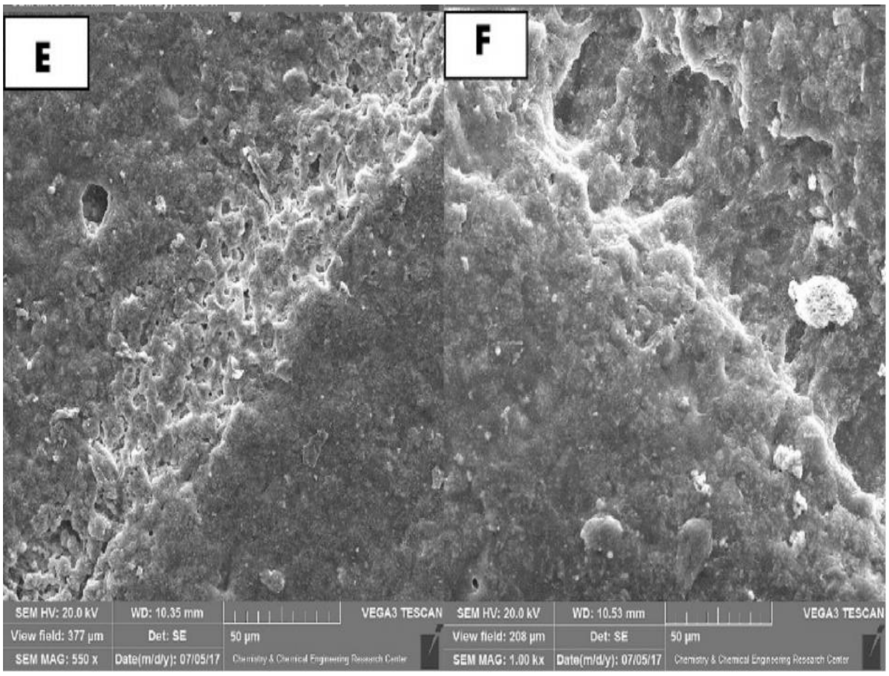

Fig.3- FESEM images of A,B,C,D,E and F [18].

Adhesion strength

As per the past examinations, it very well may be inferred that expanding the level of nanocapsule decreases the grip of the coating to the metallic surface [19], while comparable results were not see on the effect of against corrosion administrator. The eventual outcomes of security quality draw off test showed that all the changed coatings lost a part of their grasp to the substrate by growing the proportion of nanocapsule and against corrosion experts. Likewise, the preapred coatings with polyurethane demonstrated commonly higher connection to the surface and better obligation of these coatings was seen at more noticeable.

It was examined that made scratches were filled absolutely in cream coatings and corrosion deterrent was stunningly improved by utilization of against corrosion pros, while obligation of coatings to the metal surface decreased hardly.

Coating performance

Here, we audit articles related to self-healing coatings loaded with lineseed drying oil. In this assessment, linseed oil close by driers has been picked as a healing administrator on account of its film confining limit by climatic oxidation. Microcapsules with drying oil as an inside were joined by in situ polymerization. Ampleness of these microcapsules in healing of cracks in an epoxy coating and corrosion security has been delineated. Loading of linseed oil in the capsules happens at the same time during advancement of crosslinked polymer. A shell thickness of

0.2µm was gained at 250 rpm to contain 80% linseed oil. All things considered, most of the particles fall in the size range around 50µm. This is excellent for using in paints.

Mechanical stability of microcapsules

Microcapsules ought to have adequate mechanical solidarity to bear the pressure created during blending and utilization of coating. Microcapsules ought not rupture during blending and utilization of coating. They should rupture and delivery healing substances while crack is created in the coating film. Thickness of the coating, mixing velocity and mixing time are the fundamental boundaries influencing the strength of microcapsules while blending and use of coating. Impact of the apparent multitude of three boundaries on the solidness of microcapsules was concentrated by mixing microcapsules in epoxy tar arrangements of changing viscosities at various velocities for fluctuating timespans. Comparative examinations were additionally done by upsetting microcapsules in mineral turpentine oil and epoxy arrangement at fixed revolution of 200 rpm.

Corrosion resistance of self-healing coating films

Corrosion of metallic substrate happens when dampness and oxygen are shipped through the cuts or crack to the metal and coating interface. Repairing of cracks, hence, gives a compelling strategy to forestall corrosion. Execution of linseed oil as a healing agent was evaluated by uncovering examples covered with paint containing filled microcapsules to salt splash. Prior to presentation, covered surface was cross-sliced up to the metal. Control examples had the paint without microcapsules. Unrivaled corrosion obstruction execution of healed picture is because of the explanation that, linseed oil delivered from burst microcapsules flow into the crack and framed a film by oxidation polymerization with air oxygen which forestalled the entrance of dampness and air and consequently forestalled corrosion.

Linseed oil close by driers has been powerful typified in to microcapsules, having sufficient solidarity to withstand shear. The cruel morphology of microcapsule shell has given incredible securing among microcapsule and paint arrange [20]. Microcapsules in paint films delivered healing material,which during breaking healed cracks effectively with acceptable anticorrosive properties.

3.2 Microcapsules containing tung oil

It is another idea to manufacture a multifunctional coating that has double self-healing capacitie and also have self-greasing up capacities. In this examination, a multifunctional coating was created by microcapsules containing tung oil. This type of drying oil has few same properties like linseed oil.

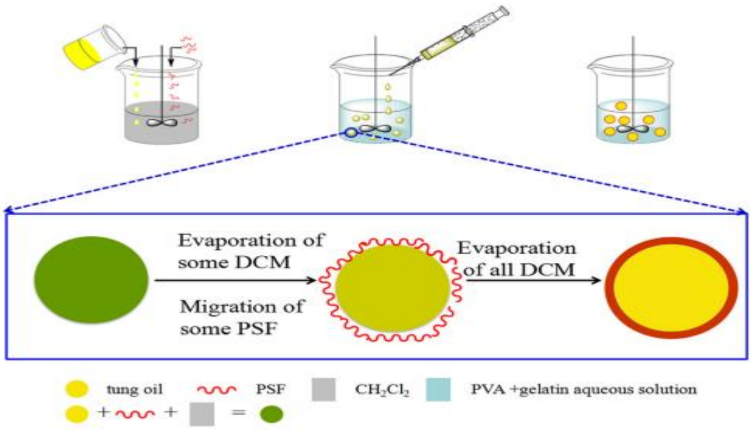

Fig.4- Microencapsulation process [21]

The crosslinking of the tung oil's particles makes the surface resistive to the water absorption. This is thoroughly utilized in paints, water absorption resistant coating, and stains. As the oil dries and fixes, the particles harden in a tight muddled arrangement, the holding also offers flexibility to the surface. In this way, tung oil can be considered as self-healing ace and self-oil. The self-healing execution was described by corrosion test and the self-lubing was overviewed by tribological test.

Corrosion resistance and self-healing performance

The self-healing execution of the coatings was evaluated by corrosion performance test. A scratches mark were set apart by extremely sharp steel on epoxy coatings and afterward the harmed coatings were left for 1 day to repair themselves. To make quicker corrosion scratched were drenched in a 10 wt% of NaCl salt solution for 1, 4 and 7 days to take into consideration corrosion.

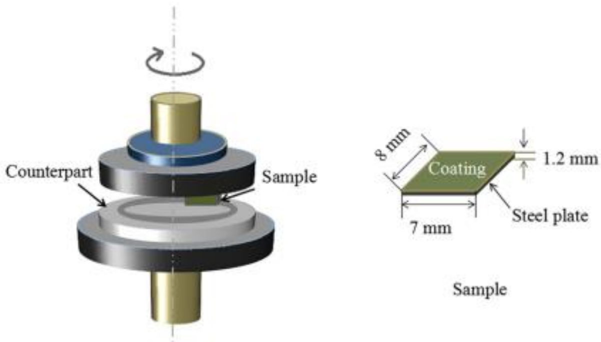

Fig.5- Test of friction and wear [21]

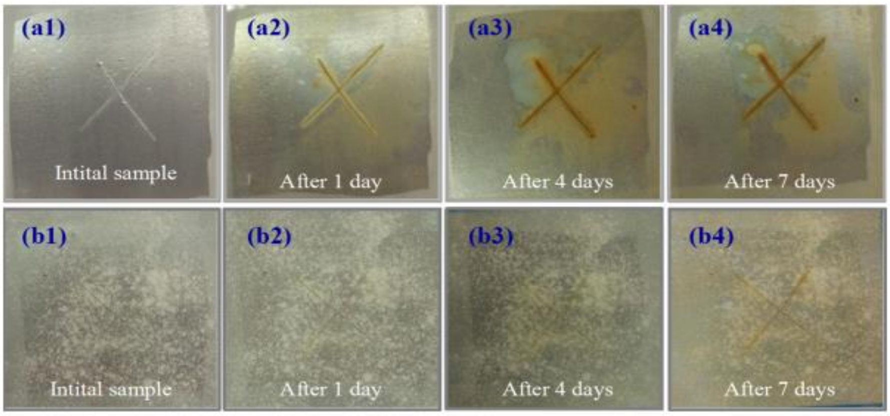

Fig.6- Scratched on epoxy coating (a1-a4) and scratched on coating of epoxy (10 wt% microcapsules) with pouring time of initial to 7th days (b1–b4). [21]

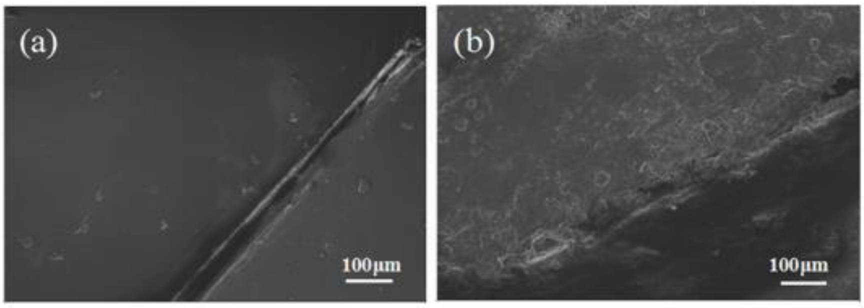

Fig.7- SEM micrographs of the scratched surface of (a) controlled coating, (b) self-healing coating (10 wt% microcapsules) [21]

The tung oil conveyed from the burst microcapsules can remove the crack normally by polymerizing in the presence of air. Undeniably, it was inspected that wire of the tung oil-stacked microcapsules can reduce the friction and wear of the coating. When the microcapsule center was furthermore extended to 15 wt% and a short time later 20 wt% then the coefficient of friction and rate of wear bit by bit extended. This miracle was credited to the reduced mechanical qualities with growing microcapsule stacking, which were seen in past examinations [21].

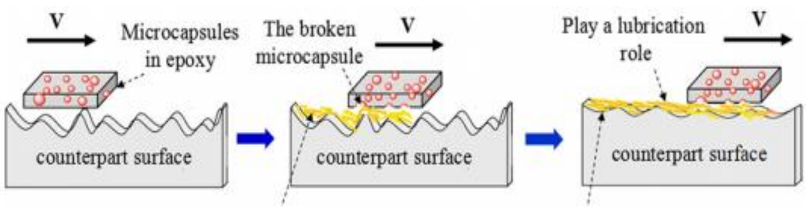

Fig.8- Self-lubricating coating techniques [21].

Despite the limit of the trade lubing up film to reduce the friction and rate of wear, the cracks microcapsules also trap wear trash. Pits addressing the broke microcapsules are indisputably watched and further results, wear was covered by the material of broken microcapsules. The lessening in the proportion of wear as a result of catch through the depressions weakened the harsh effect of the wear as a different body in interaction, which similarly reduced the friction and rate of wear. Microcapsules containing tung oil improved wear restriction similar with the unadulterated epoxy coatings.

3.3 Castor oil based self-healing microcapsules

Castor oil is another type drying oil which is easily available in rural. In past it was used to protect the costly wooden door by direct applying of oil the surface. It has good drying performance. Thus Castor oil attracts to use it in a coating with self-healing materials. Castor-oil-is a modest, naturally cordial, and profoundly spread waterborne dispersant. As of late, as the natural security approaches are progressively exacting, castor have quickly transform into the focal point of the coatings because of their numerous preferences, for example, low VOCs emanations, inexhaustibility, biodegradability and great biocompatibility [22]. Be that as it may, the presentations of long unsaturated fat of castor oil bring about inadmissible mechanical properties such as, modulus of elasticity and hardness, restricting their more extensive applications [23]. Particularly, for those coating with high castor oil content the restrictions are more critical. These issues can be successful overwhelmed by manufacturing natural inorganic core-shell mixture structure.

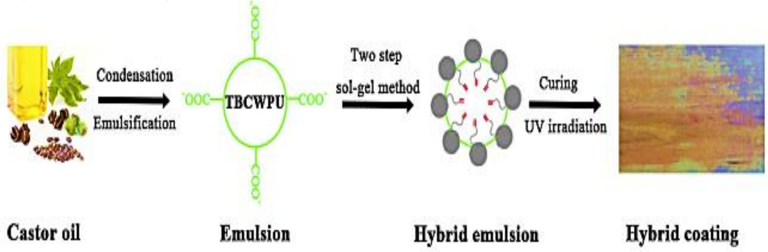

Fig.9- Process for preparation of Castor oil shell-core hybrid coating[24].

The wettability of hybrid films

3-(methacryloxy)propyl trimethoxy silane (γ-MPS) and tetraethyl orthosilicate (TEOS) were added with warm water and then properties of films is assessed. Table 3 is showing the water contact angle with different additives.

Table 3 Water contact angles of hybrid films with different components

Sample Name	Contact Angle (^{0})	Additives
F-S1	72.5	Neat Castor oil
F-S2	53.5	20 wt% of γ-MPS
F-S3	66.0	16 wt% of γ-MPS
F-S4	73.6	10 wt% of γ-MPS
F-S5	80.2	20 wt% of TEOS

Water resistance of hybrid films

Table 4 is presenting the water protections of the cross breed films were assessed by water retention tests.

Table 4 Water absorption test results

Sample Name	Water absorption (%)	Soaking Time (days)	Additives
F-S1	22	2	Neat castor oil
F-S2	7.5	2	20 wt% of γ-MPS
F-S3	14.8	2	16 wt% of γ-MPS
F-S4	12.5	2	10 wt% of γ-MPS
F-S5	16	2	20 wt% of TEOS

Evaluation of mechanical characteristics

The mechanical characteristics were evaluated and are taken for audit. Besides, with the expansion of the γ-MPS content, the yield quality, elasticity, Young's modulus, and hardness expanded, while the lengthening at break diminished to a greater extent.

4 Conclusions

In the previous years, critical inventive advancements have been made in the examination field of self-healing materials microencapsulated with normal drying oil, their planning and portrayal. Notwithstanding, at some point its application has restriction for fix the harmed. The self-healing strategies have opened the path in the field of polymer composites. Distinctive self-healing methodologies have been essentially applied to polymer, composite and coating of metallic materials, anyway little consideration has been paid to utilize drying oil to dodge utilize characteristic non-biodegradable polymers. We inspected the sciences of self-healing epoxy containing with various normal drying oil and presented instances of self-healing epoxy stacked with common oils. The exploration in the self-healing of epoxy is still in its initial advancement stage. The self-healing systems in epoxy tar depend on various polymerization component as talked about in this article. In the field of polymer and coating materials, there is gigantic open door for additional advancement and improvement of new self-healing epoxy. In this examination, we exhibit that rapeseed oil is the most encouraging added substance to accomplish water repellency in the lime glue. The degree of saturation of the fatty acids strongly determines their chemical reactivity, and according to this aspect, linseed oil could be regarded as the most chemically reactive oil used in this study since it comprises the highest amount of C–C double bonds. Nevertheless, rapeseed oil has granted higher hydrophobicity than linseed oil to the lime paste. Hence, oils with a higher amount of monounsaturated fatty acids may be more effective in imparting hydrophobicity. Another positive outcome of the rapeseed oil addition to lime is that the rounded voids developed were evenly distributed in the matrix and showed size diameters within a close range (10–50 μm) even when the amount of oil was higher, whereas linseed and stand oil promoted a heterogeneous distribution of pores with a much wider range of sizes (10–500 μm).

Innovative researches in the field of self-healing epoxy would benefit the new advanced high-strength polymer or coating materials. The future progress in self-healing epoxy resins will depend upon the research and development of advanced techniques offering formation of advanced polymer composite materials.

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