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Sustainable Self-Healing Coatings: Optimizing Microencapsulation of Biodegradable Linseed and Hemp Seed Oils for Enhanced Corrosion Protection

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Research Article

Abstract − Corrosion is one of the biggest challenges in metal surfaces, especially when scratches and impacts damage the coating. Self-healing agents in the coating ensure long-term protection, effectively shielding the metal from corrosion. However, these materials are not environmentally friendly in general. To improve sustainability, we propose encapsulating renewable and biodegradable natural drying oils (linseed and hemp seed oils) to enhance the self-healing properties of the coatings. In-situ polymerization of these urea-formaldehyde microcapsules was performed at 60 °C using different stirring rates (200, 300, and 400 rpm). The structural, morphological, and thermal analyses were carried out by using Fourier Transform Infrared Spectrometer (FTIR), Scanning Electron Microscope (SEM), and Thermogravimetric Analysis (TGA). The particle size and oil content measurements were also performed. It was observed that a 300-rpm stirring rate resulted in optimum morphology, particle size, and oil content. 10 wt% microcapsules containing pure epoxy coatings were successfully applied to metal surfaces. It was observed that coatings with microcapsules provided better surface protection compared to pure coatings, and linseed oil-loaded microcapsules outperformed hemp seed oil-loaded microcapsules. These materials hold promise for future self-healing applications that are both effective and environmentally friendly.

Keywords − *Corrosion protection, self-healing, encapsulation, urea-formaldehyde microcapsules, drying oils*

1. Introduction

Metals are used in many fields, such as chemistry, industry, transportation, construction, paint, electronics, and medical implants. The main problem for metals is surface wear or corrosion, which destroys the surface [1]. In 2013, the global cost of corrosion was estimated at US$2.5 trillion, representing 3.4% of the worldwide gross domestic product, the total value of goods and services produced worldwide within a year [2]. This situation creates a major economic problem and leads to environmental destruction. Corrosion contaminates nature, water, and air, accumulates in nature, and threatens the health of living beings [3]. Coating, painting, and lubrication have been used to reduce the effects of damage caused by corrosion on the material corrosion [4]. However, if the surface is damaged in any way, the exposed metal will inevitably corrode. In recent years, self-healing polymer coating systems, inspired by living organisms' self-healing mechanisms, have been used to prevent corrosion and extend the life of metal surfaces. Self-healing agents, encapsulated in micron-sized capsules, are protected from degradation and uniformly distributed across the surface. Promising results have

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been achieved with self-healing polymers in preventing surface corrosion caused by wear over time [5], mainly through methods that involve breaking the bonds of an encapsulated polymer and filling them with the help of a crosslinker [6], frequently used to develop technologies aimed at extending material longevity. Self-healing coating using various polymers is used in many sectors, such as agriculture, food, packaging, biomedical, metal, and electronics [7]. Product examples include cell phones, varnishes, boat hulls, and adhesives [8].

Using bio-based and biodegradable materials tackles waste management challenges at the end of their lifecycle and significantly lowers the carbon footprint by maintaining a closed carbon cycle. With this objective, catalyst-free, natural drying oils, and non-toxic polymers are offered to achieve a successful self-healing system. Urea-formaldehyde (UF) microcapsules, with self-healing properties to prevent corrosion of metal surfaces, were synthesized that contain natural oils, linseed oil, and hemp seed oil, produced from linseeds and hemp seeds (Figure 1), can be oxidized at room temperature. The reasons for using urea-formaldehyde as a capsule shell include impermeability, flexibility, good penetration resistance, and durability [9]. Epoxy is widely used to coat metal surfaces. Linseed oil, a frequently used drying oil, has a high molecular weight and high fatty acid content and was selected as a curing agent by completing cross-linked polymerization in a short time [10]. Hemp seed oil, extracted from hemp seeds, is reported as a successful material to prevent corrosion [11].

Figure 1. (a) Linseed and (b) hemp seed, whose oils serve as natural self-healing agents in the study

The microcapsules were synthesized via in-situ polymerization using stirring rates of 200, 300, and 400 rpm, and their particle size, oil content, and structural, morphological, and thermal properties were analyzed. Based on these evaluations, an optimal stirring rate of 300 rpm was determined. The self-healing properties of the oil-filled microcapsules were assessed using a salt spray test, demonstrating that the epoxy coating with microcapsules effectively prevented corrosion compared to the pure epoxy coating. As the materials used were easily accessible and inexpensive, it has high potential for rapid realization in industrial applications. These materials can be used in many applications, such as metals, electronics, artificial tissue, and implants.

2. Materials and Methods

Polyvinyl alcohol (PVA) (partially hydrolyzed, %85-89) was kindly provided from Beta Kimya AŞ. Sodium dodecyl sulfate (SDS) (%90) was purchased from Sigma-Aldrich, USA. Urea (99%), ammonium chloride (99%), and formaldehyde (37 wt% aq) were purchased from ISOLAB, Germany. Resorcinol (98%), NaOH and HCI (37%) were purchased from Merck, Germany. Slim as epoxy resin and its hardener (used a 2:1 (v/v) ratio) were purchased from Resinin, Mersin, Türkiye. Linseed oil and hemp seed oil were purchased from Mecitefendi, İzmir, Türkiye. All chemicals were used without any purification.

2.1. Synthesis of the Urea-Formaldehyde Microcapsules

Based on the study of Abdipour et al. [12], UF-based microcapsules were synthesized by in-situ polymerization in an oil-in-water emulsion. First, 0.5 g of PVA was dissolved in 300 mL of water in a 500 ml round flask with

two necks at 60 C. Heating was stopped. 0.15 g of SDS was added. PVA particles were mixed at a certain mixing rate for 2 hours -three alternative mixing rates (200, 300, and 400 rpm). Then, the solution received 5 g urea, 0.5 g resorcinol, and 0.5 g of ammonium chloride. By using aqueous solutions of 0.1 N NaOH and 0.1 N HCl, the pH was adjusted to 3.5. 15 mL of linseed oil or 15 mL of hemp seed oil were introduced with a micropipette at a 1 ml/min rate to create an emulsion, which was then allowed to stabilize for 15 minutes. To keep the molar ratio of formaldehyde to urea to 1.9:1, 11.8 mL of formaldehyde solution was added to the emulsion [13]. The reaction medium was slowly heated to 55 °C and kept at this temperature for 4 h [14]. The suspension was then cooled to room temperature. After phase separation, vacuum filtration isolated the capsules from the suspension. They were then rinsed with distilled water and xylene to eliminate residual impurities. The microcapsules were stored in an xylene and distilled water (1:2 by volume) emulsion to prevent agglomeration.

2.2. Determination of Oil Content in the Microcapsules

The amount of core material (healing agent) in the microcapsules was measured using the extraction method [15]. For this purpose, 1 g of microcapsules (m_1) were mixed with 10 mL acetone and sonicated for 1 min. The suspension was passed through ultrafine filter paper to remove the remaining shell materials. The filtrate was then rinsed several times with acetone and dried in a vacuum oven at 40 °C until steady mass (m_2). (2.1) was used to calculate oil content.

$$\text{Oil content (\%)} = \frac{m_1 - m_2}{m_1} 100 \quad (2.1)$$

2.3. Preparation of Epoxy Resin Coating and Salt Spray Test

At ambient temperature, microcapsules (10 wt%) were transferred into the uncured epoxy resin and stirred using a glass stirrer for 5 min slowly to prevent the formation of bubbles until the microcapsules were homogeneously distributed. Before the coatings were applied, the metals were cleaned using a metallography sample-sanding and polishing device. The microcapsule in epoxy was spread on the metal specimens slowly without causing air bubbles. The specimens were maintained at room temperature for 6 h, then cured for 1 h at 80 °C. A pure epoxy resin coating was prepared as a control sample. Three repeated incisions at three different depths were made on a metal sheet with a scalpel to observe the self-healing mechanism. A salt spray test was then performed. A 5 wt% saline solution was sprayed on the metal sheet at regular intervals as to be 4 times a day for 4 days to assess the corrosion resistance of the coated sheets, which was a rather high salt percentage (sea water salt percentage: 3.5%) to simulate harsh conditions and accelerate the rusting. As the desired level of corrosion had not been achieved, the experiment was repeated with deeper cuts after 4 days to further accelerate the rusting process.

2.4. Characterization

A Phillips XL30 SFEG scanning electron microscope determined the surface morphology of the samples. A gold layer was coated onto all samples to minimize charging effects and then analyzed at an accelerating voltage of 15 kV. To ensure comprehensive imaging, at least three separate areas were assessed. Linseed and hemp seed oil-loaded UF capsules' thermal stability was characterized using Metter Toledo TGA/SDTA851e. The heating rate was 10 °C/min in the 20 – 720 °C temperature range. Particle size was determined using a Malvern particle-size analyzer. Structural analyses of the oils and oil-loaded microcapsules were carried out using a Perkin Elmer 100 FTIR spectrometer. An optical microscope was used to determine the distribution of the microcapsules in the epoxy coating, releasing the oil after forming the scratch on the coating.

3. Results and Discussion

3.1. Microcapsules at Different Phases

The text linseed oil and hemp seed oil containing microcapsules can be denoted as KT and KV, respectively. The numbers beside them express the rpm value at which the microcapsules were synthesized. First, the microcapsules were characterized at the top and bottom phases in a 1:2 emulsion of xylene and water (Figure 2) (Top phase: xylene, bottom phase: water). Particle sizes at the phases were investigated at the stirring rate of 300 rpm. The following characterizations will further discuss the reason for selecting this stirring rate.

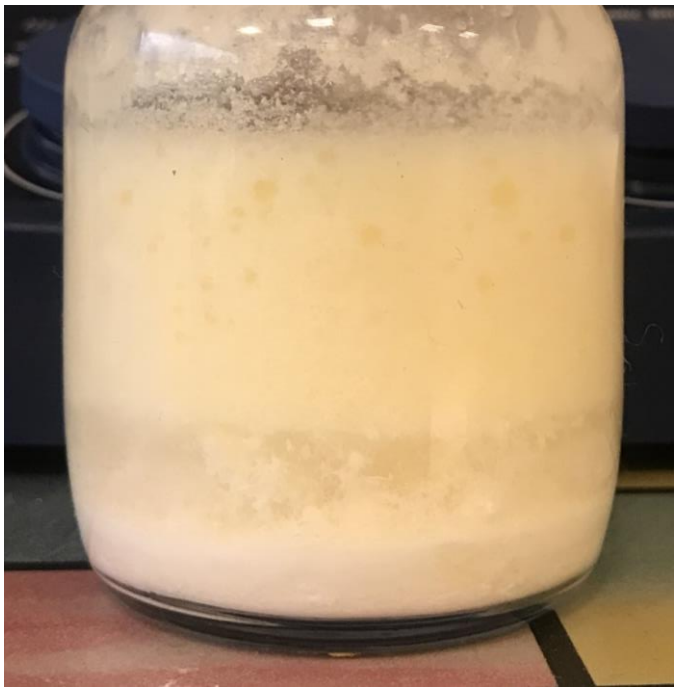

Figure 2. The general appearance of hemp-containing microcapsules in xylene-water emulsion.

Based on the general appearance of the microcapsules (Figure 1), regardless of the oil type used, the xylene phase contained a greater quantity of microcapsules, which appeared more yellowish, likely due to the oil content. In contrast, the lower phase (water) had fewer microcapsules, and they exhibited a whiter color.

Particle size analysis of the phases, as shown in Table 1, revealed some significant differences. The top phase of linseed oil and hemp seed oil microcapsules had average particle sizes of 80.73 μm and 120.18 μm, respectively, while the lower phase of microcapsules measured 39.14 μm and 14.46 μm. SEM images (Figure 3) also revealed the size and shape differences of the microcapsules at the top and bottom phases. It was observed that the capsules at the top had larger particle sizes, which can enable more oil storage, which is crucial for enhancing their crack-sealing capability in the study. In contrast, smaller particles at the bottom of the solution may be less effective in storing oil. Therefore, the microcapsules at the xylene phase were chosen for further characterization.

Table 1. Particle size of synthesized capsules at different positions in the solution

Capsule Location	Particle Size (μm)
Linseed top oil phase	80.62 ± 4.17
Linseed oil bottom phase	39.14 ± 4.05
Hemp seed oil top phase	120.18 ± 18.71
Hemp seed oil bottom phase	14.46 ± 6.94

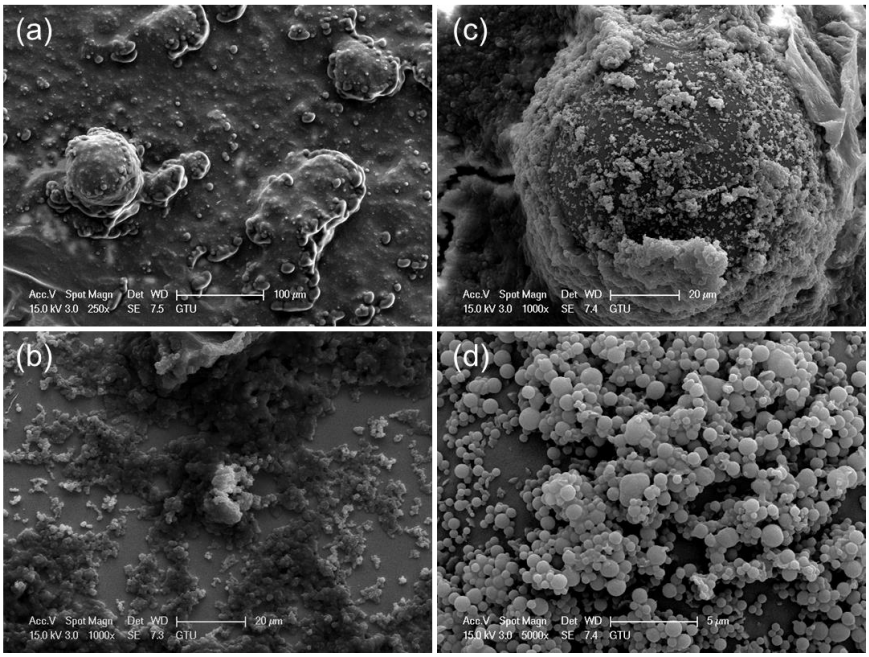

Figure 3. SEM images of (a, b) linseed oil and (c, d) hemp oil-loaded microcapsules at the (a, c) top phase and (b, d) bottom phase, respectively

3.2. Chemical Structure of the Microcapsules and Oils

The FTIR spectrophotometer performed the structural analysis of the microcapsule materials. Here, FTIR peaks of microcapsules filled with linseed oil and hemp seed oil prepared at 300 rpm were obtained as precisely overlapping each other (Figure 4). The peaks of the microcapsules matched well with urea-formaldehyde resin where the peak at 3300 cm^{-1} is the N-H stretching, the peaks between 2850-2972 cm^{-1} correspond to CH stretching of CH_2, CH_2OH, and N-CH_2, the peak at 1741 cm^{-1} occurs due to C=O stretching of formaldehyde (also that of linseed oil), the peaks at 1616 and 1535 cm^{-1} are results of C=O stretching of amide I and C-N and N-H deformation of amide II, 1372 and 1240 cm^{-1} peaks belong to C-H stretching and OH deformation of CH_2OH group. 1158 cm^{-1} is due to asymmetric stretching of N-CH_2 (and also probably the C-O-group of oil [16]), and 1016 cm^{-1} occurs because of C-O stretching in the methyl group [17]. Plus, as the microcapsules were crashed during FTIR analysis, the peaks belonging to oils were also visible, such as 731, 1108, and 1450 cm^{-1} (shown in red) as being the corresponding peaks of cis CH=CH (of linseed oil), C-O and CH_3 groups of the oils [16].

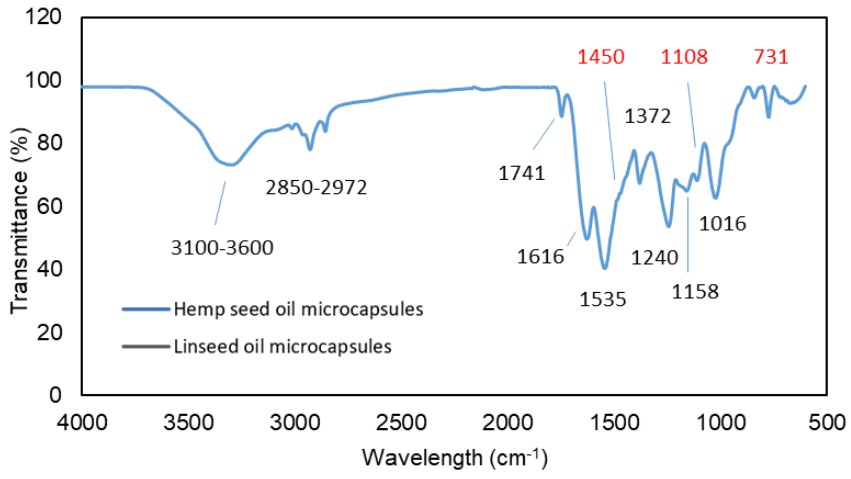

Figure 4. FTIR spectrum of UF microcapsules filled with hemp seed oil and linseed oil prepared at 300 rpm. peaks shown in red belong to oils only

Linseed and hemp seed oil were also structurally characterized (Figure 5). The oils contained the same characteristic peaks on the spectrum where 2971 cm^{-1}, 2918, and 2850 cm^{-1} peaks correspond to the vibrations of =C-H, -CH_3, and –CH_2– bonds, respectively. 1746 cm^{-1} peak is the C=O stretching, 1640 cm^{-1} peak occurs because of the unsaturated C=C bonds, 1366 and 1451 cm^{-1} peaks belong to –CH_3 groups, 1161 cm^{-1} peak belong to C-O– group, 722 cm^{-1} is the vibration of cis CH=CH double bonds [16] which was shifted to 731 cm^{-1} in the UF capsule.

The slight difference between linseed oil and hemp seed oil is the peak at 722 and a bump on the 755 peak as the vibration of cis CH=CH bonds [16] and =CH bending [18] occurring due to the double bonds that exist in the fatty acid structure. This difference is probably because of the difference in the fatty acid type and content of the oils. Linseed oil contains more linolenic acid with three double bonds. In contrast, hemp seed contains more linoleic acid that has two double bonds (Linseed oil: 53.21% linolenic acid, 17.25% linoleic acid, 18.51% oleic acid, etc. [19]. Hemp seed oil: 58.71% linoleic acid, 16.81% linolenic acid, 13.05 oleic acid, etc. [20]) linseed oil had slightly showed higher intensity of those mentioned peaks.

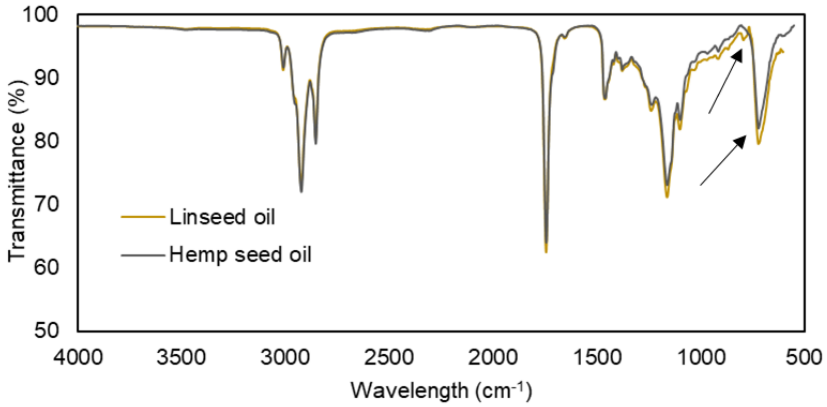

Figure 5. FTIR spectra of linseed oil and hemp seed oil

3.3. Effect of Stirring Rate

3.3.1. Structural Properties

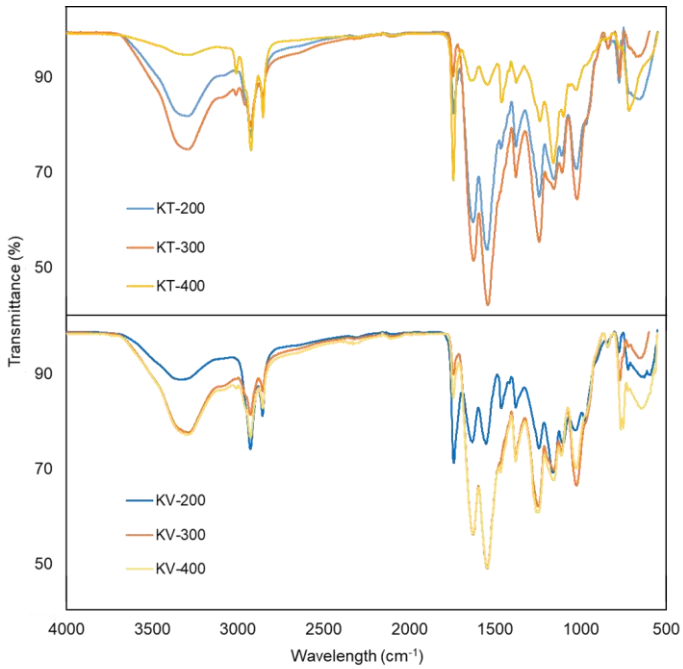

Figure 6. FTIR spectra of linseed oil (up) and hemp seed oil (down) containing microcapsules prepared at different stirring rates

The effect of stirring rate on the structural properties of the microcapsules is given in Figure 6. For this, we focus on the peaks 3000-3500 cm^{-1} and 1740 cm^{-1} belonging to the N-H group of UF resin and C=O oil group stated earlier. For linseed oil containing microcapsules, more oil was observed for microcapsules prepared at 400 rpm than other stirring rates. The least amount of oil and the highest amount of UF was observed for KT-300, which may indicate strong cross-linking of UF microcapsule. (The analysis of oil percentage will be further discussed.) For hemp seed oil containing microcapsules, while similar results were obtained for 300 and 400 rpm, the highest amount of oil was observed for 200 rpm samples.

3.3.2. Morphology and Particle Size Distribution

On the self-healing ability, microcapsules should have a spherical morphology with an oil-containing core and a stable particle size. The effect of stirring rates on the morphology of the linseed and hempseed-containing microcapsules is shown in Figure 7. At 200 rpm, the linseed oil microcapsules appeared as rather large chunks, and upon magnification, some bumps were visible, which may indicate combined microcapsules. At 400 rpm, instead of chunks, large and combined spheres were observed, and close magnification revealed a broad oily surface with no distinct microcapsules, indicating that no microcapsules were formed to store the oil, which is consistent with the high oil content observed in the FTIR analysis for this sample. However, at 300 rpm, the desired spherical microcapsules were achieved with sizes that were consistent with each other. For hemp seed oil containing microcapsule preparation, large spheres were formed for both 200 and 400 rpm stirring rates, a close magnification showed no small microcapsule formations on these spheres. Whereas, like linseed microcapsules, the 300 rpm stirring rate also resulted in spherical microcapsule formations. However, hemp seed oil microcapsules exhibited some size variation and appeared stickier than those in the linseed oil system. SEM findings revealed that the microcapsules produced at a stirring rate of 300 rpm were more homogeneously distributed and spherical. This successful microcapsule formation enables efficient release of the agents thereby enhancing the self-healing performance of the coating.

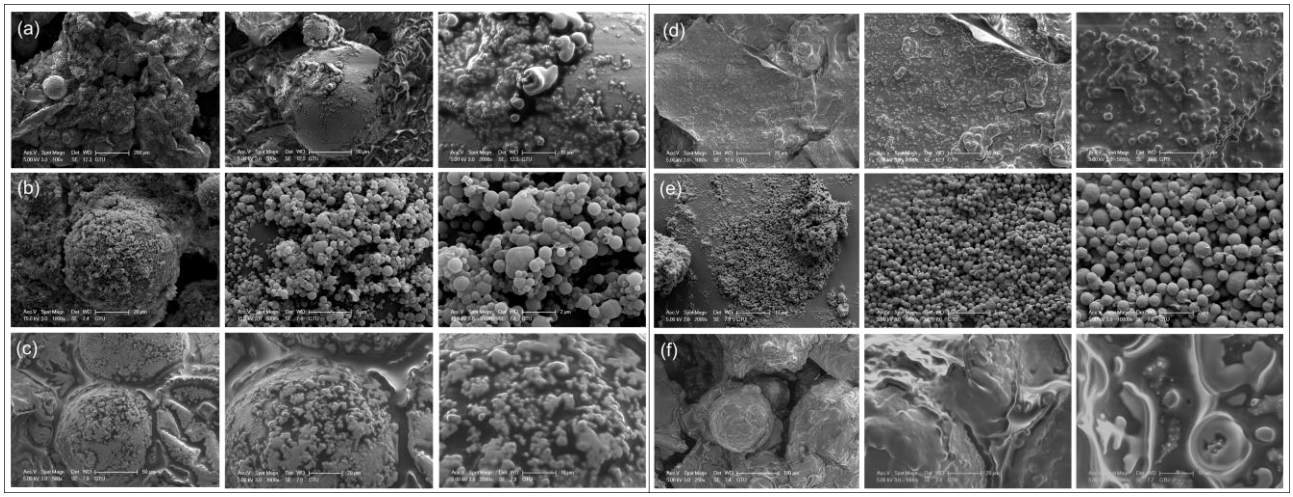

Figure 7. SEM images of linseed oil-loaded capsules at (a) 200, (b) 300, (c) 400 rpm and hemp seed oil-loaded capsules at (d) 200, (e) 300, (f) 400 rpm

The particle size analysis of the microcapsules prepared at different stirring rates is given in Figure 8. For both oil systems, 200 and 400 rpm produced larger microcapsules (or urea-formaldehyde resins in various forms) with greater size variability, as confirmed by SEM images where larger chunks were predominantly observed and at 300 rpm linseed and hemp seed oil containing microcapsules resulted in sizes of 77.25 and 116.30 μm, respectively, where hemp seed oil microcapsules showed a larger deviation which was also detected in SEM images. These size differences are also supported by the optical microscope images of KT-300 and KV-300, distributed in an epoxy matrix, in Figure 9, where linseed oil microcapsules are smaller than hemp seed oil microcapsules. Here, the oil in the microcapsules also appears clearly as a light hue.

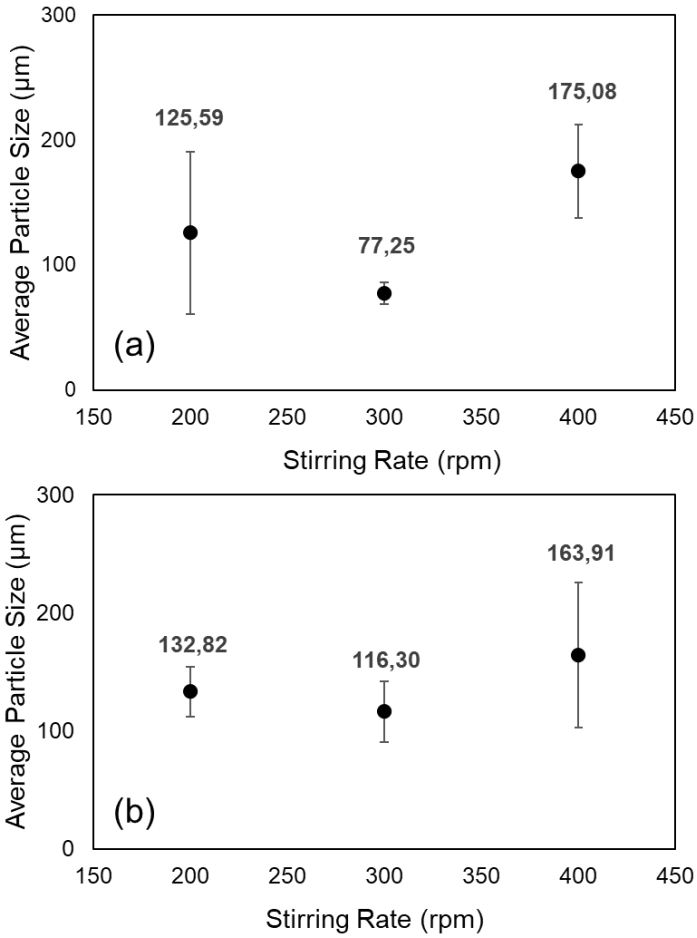

Figure 8. Average particle sizes of the (a) linseed oil and (b) hemp seed oil-loaded microcapsules prepared at 200, 300, and 400 rpm

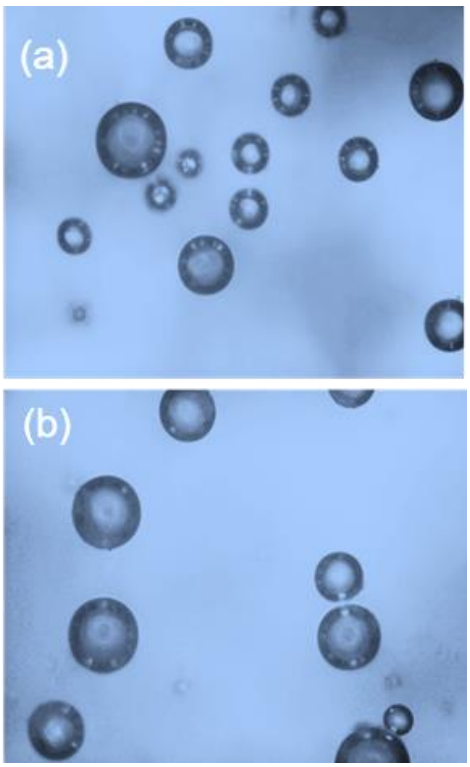

Figure 9. Optical microscope images of (a) linseed oil and (b) hemp seed oil-filled microcapsules prepared at 300 rpm distributed in epoxy (×50 magnification)

In the study of Behzadnasab and colleagues, synthesis was performed at 500-1500 rpm, and microcapsules of 16-181 μm sizes were obtained [21]. Abdipour and colleagues report stirring rate from 300 to 900 rpm decreased particle sizes from 74 to 62 μm [12]. Hatami Boura and colleagues show that 400 rpm and 600 rpm stirring rates resulted in 75 and 50 μm. However, only two stirring rates were tested [22]. While the particle size decrease between 200 and 300 rpm aligns with previous studies, an increase in microcapsule size was observed at 400 rpm. These findings suggest an optimal stirring rate beyond which particle size begins to increase. SEM images of the synthesis at 400 rpm indicate that deformation and probably agglomeration occurred in the microcapsules, increasing particle size. Icduygu and colleagues indicate that at high stirring rates, the frequency and intensity of collisions between microcapsules increase during encapsulation, leading to agglomeration [23]. As a result, to prevent agglomeration and ensure successful microcapsule formation, it was found that an optimal stirring rate is essential.

3.3.3. Oil Content of the Microcapsules

Table 2. The oil content of microparticles, both linseed oil (KT) and hemp seed oil (KV)-loaded microcapsules at 200, 300, and 400 rpm

Capsule Type	Oil (%)
KT-200	7.56
KT-300	65.00
KT-400	63.52
KV-200	9.46
KV-300	68.15
KV-400	52.05

The oil content of microcapsules is crucial for effective self-healing performance and should be maximized in well-formed, cross-linked spherical microcapsules. According to the results in Table 2, for both oil systems, the lowest oil content belonged to the 200-rpm stirring rate, which is less than 10%. This low oil content was also confirmed in the FTIR spectrum of hemp seed oil containing microcapsules prepared at 200 rpm. However, when the stirring rate was increased to 300 rpm, the oil content significantly rose to 65% and 68.15%, representing significant increases of 740% and 620% for linseed and hemp seed oil-loaded microcapsules compared to those prepared at 200 rpm. This is expected, as a properly cross-linked microcapsule structure was achieved (SEM images) at the stirring rate of 300 rpm, allowing maximum oil storage. The oil content difference between linseed oil and hemp seed oil-loaded microcapsules at 300 rpm may be due to their particle size reported earlier (77.25 and 116.30 μm, respectively), as larger particles can capture more oil inside. KT-400 and KV-400 also contain rather high amounts of oil. However, according to SEM images, this oil is probably not properly trapped in microcapsules, as the obtained microstructures were more likely disordered. Abdipour and colleagues achieved oil contents ranging from 60% to 90% at stirring speeds of 300 to 900 rpm [12]. Behzadnasab and colleagues reported oil contents between 63% and 77% for stirring rates of 500 to 1500 rpm in linseed oil-urea formaldehyde microcapsules [21]. Both studies demonstrated that oil content was inversely proportional to the stirring rates used during encapsulation. Here, similar to the microcapsule size situation, an optimum stirring rate (300 rpm) was found for maximum oil content (65% and 68% for linseed and hemp seed oil-loaded microcapsules, respectively) in the microcapsules.

3.3.4. Thermal Properties

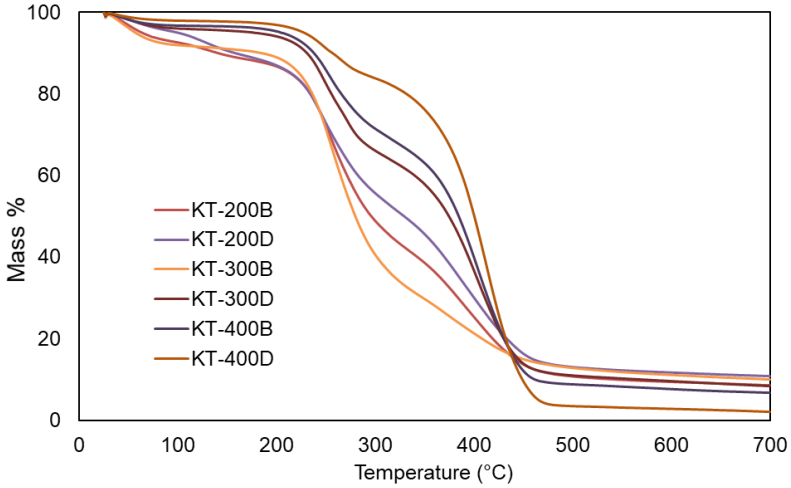

Figure 10. TGA thermograms of linseed oil containing microcapsules prepared at different stirring rates (extracted shells: B and non-extracted microcapsules: D)

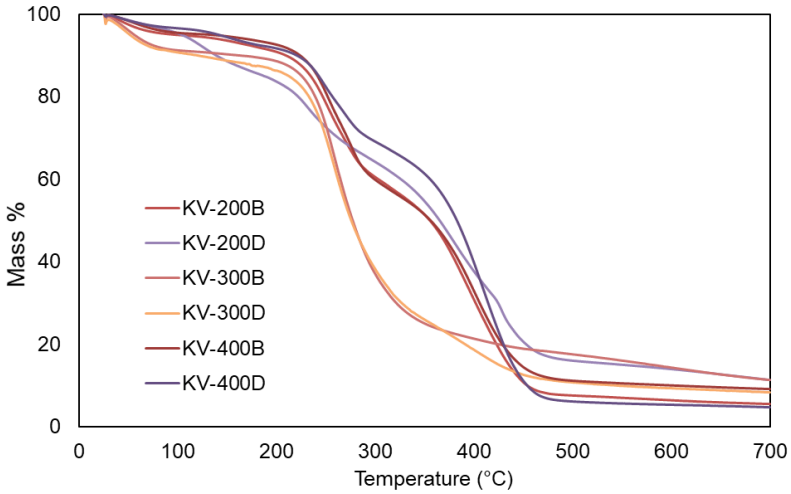

Figure 11. TGA thermograms of hemp seed oil containing microcapsules prepared at different stirring rates (extracted shells: B and non-extracted microcapsules: D)

Thermal degradation results of UF microcapsules (D), extracted UF shells (B) prepared with linseed oil (KT), and hemp seed oil (KV) as a function of stirring are given in Figures 10 and 11. The degradation of microcapsules consists of three steps—mass loss around 100 °C results from evaporation of water and unreacted formaldehyde. The mass loss between 200–300 °C is because of the evaporation of formaldehyde in the microcapsules. The degradation between 300 and 400 °C is probably due to the evaporation of hemp seed and linseed oils, as their boiling points are around 316 °C. The following mass loss after 400 °C is because of the oxidative removal of nitrogen, oxygen, hydrogen, and other elements, leading to the carbonization of the cross-linked UF shell. [24]

Although Yang et al., who reported the microencapsulation of isophorone diisocyanate, found similar thermal properties for all microcapsules prepared at different stirring rates, we observed apparent changes in the thermal stability as a function of stirring rates. [25] For microcapsules containing linseed oil, a noticeable difference was observed for each stirring rate between the oil-containing and extracted microcapsules, with the oil-containing microcapsules exhibiting higher thermal stability at 300–400 °C. When we investigate thermal stability as the shift of the initial degradation temperatures, except the extracted shell of KT-300, there is an increasing thermal stability trend with the increasing rpm values. For hemp seed oil containing

microcapsules, similarly, microcapsules prepared at 400 rpm had higher initial degradation temperatures (so higher thermal stability) than those prepared at 300 rpm. However, the results for microcapsules prepared at 200 rpm were less stable than those for linseed oil microcapsules. This instability is likely due to the improper formation of spherical microcapsules and the significantly lower oil content than those prepared at 300 and 400 rpm. A suitable amount of oil in the microcapsules with proper spherical structure guarantees a sufficient healing agent to discharge and repair cracks.

Both for microcapsules prepared with linseed and hemp seed oils at 300 rpm, the mass loss characteristic of oils at 300–400 °C was less observable compared to microcapsules prepared at other stirring rates, probably because the optimum cross-linking degree and higher thickness resulted in the strong entrapment of oil inside the UF microcapsules. For both oil systems, the stirring rate of 400 rpm resulted in the lowest mass loss at the same degradation temperature region. This is likely due to the failure to achieve a properly spherical microcapsule structure at this specific stirring rate and high oil content, leading to the easy release (or already exposed) of oil on the UF surface.

3.4. Evaluation of Self-Healing Process

Based on the previous findings, microcapsules prepared at 300 rpm were chosen for self-healing studies. 10 wt% of capsules were mixed into the epoxy coating, and optical microscopy was used to examine their distribution (Figure 12). After mixing with epoxy, the microcapsules retained their spherical shape and oil core within the coating. Additionally, linseed oil-loaded microcapsules (Figure 12a) demonstrated better distribution in the epoxy matrix than hemp seed oil-loaded microcapsules (Figure 12b).

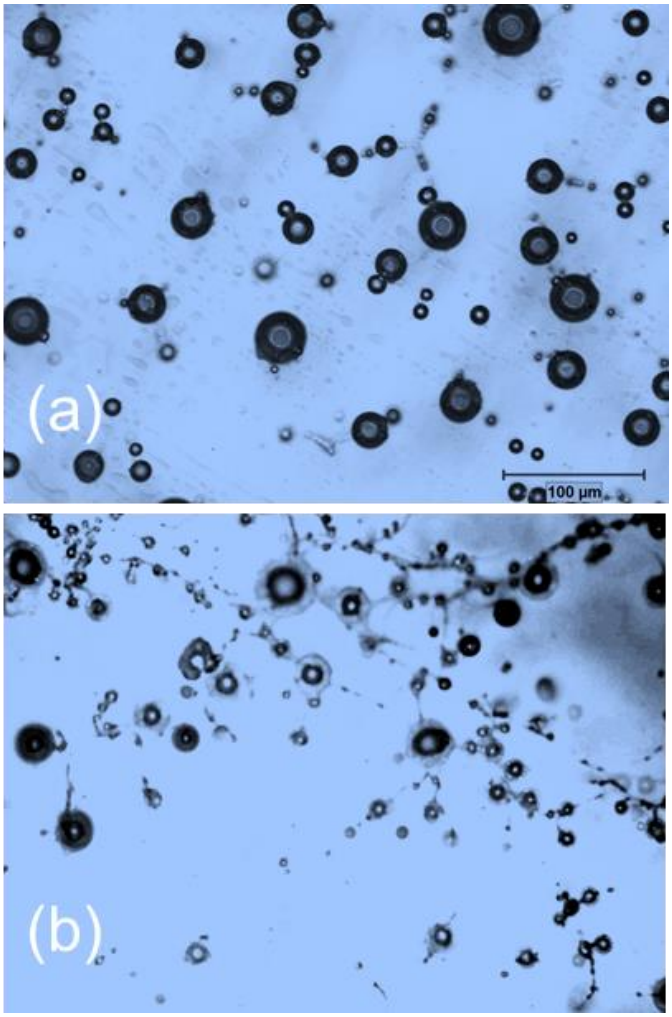

Figure 12. Optical microscope images of 10% (a) KT-300 and (b) KV-300 capsules in epoxy coatings, respectively

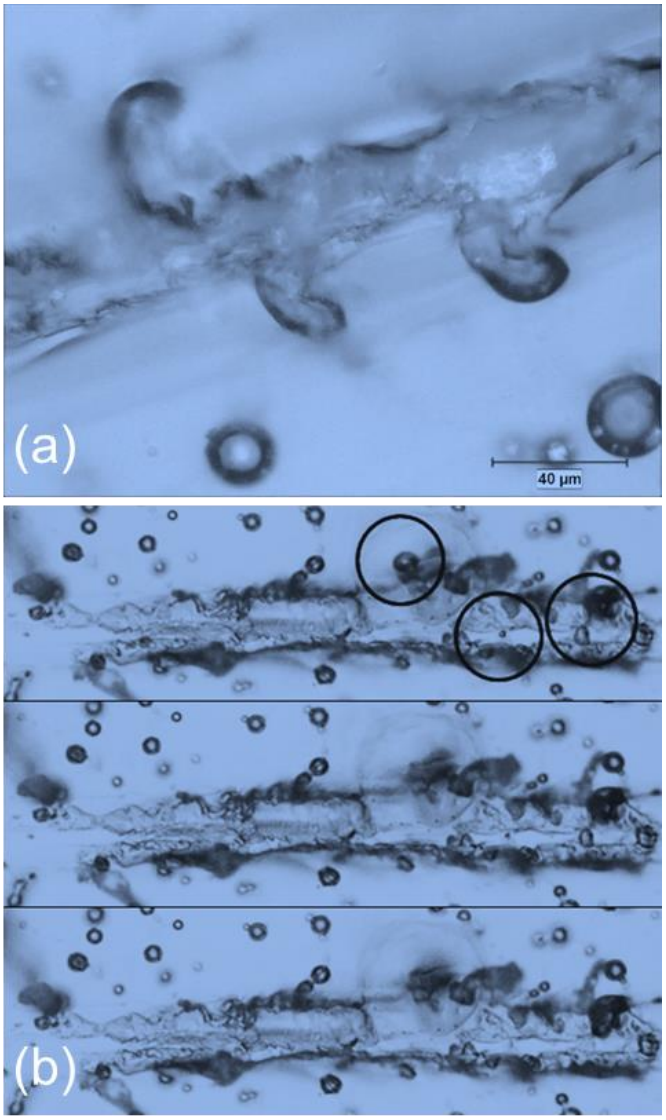

Figure 13. (a) The moment at which oil is released after scratching the epoxy surface containing linseed oil-loaded microcapsules. (b) Optical microscope images of coating filled with hemp oil-loaded microcapsules were taken during 20 minutes of observation after the scratch

Under optical microscopy, the incision in the coatings was observed in (Figure 13a). After the scratch, the oil was released as some microcapsules burst and disrupted their shell structure, causing the oil to escape gradually due to internal pressure (Figure 13b). Once the capsules are broken, oils are released and fill the scratch. After that, oil oxidation occurs. Since hemp seed and linseed oils are drying oils, the oil oxidizes in the air to form a protective layer in the scratch. The self-healing properties of the coating are achieved through the function of these natural oils. However, not all regions contained microcapsules. Proper distribution and quantity of capsules in self-healing coatings are crucial, as uneven dispersion can result in areas that lack self-healing capability [26].

3.4.1. Salt Spray Test

A salt spray test was conducted to visually assess the self-healing performance to induce corrosion on the coatings. For this, manual scratches were applied to coatings prepared with either only epoxy coating as a control epoxy coating containing 10% linseed and hemp seed oil microcapsules, separately (Figure 14).
On the second day of the test, rust started to appear on areas without epoxy coating, while only small rust spots were observed on the inner parts of the pure epoxy coating. In contrast, the coatings with microcapsules did not show such rust formation. On the fourth day of the salt test, rust began to appear at the scratches on the

pure epoxy coating, while no rust was observed on the coatings prepared with both linseed oil and hemp seed oil loaded microcapsules. All microcapsule-containing coatings effectively prevented corrosion in the salt-spray test compared to epoxy coatings without capsules.

After the first four days, the corrosion experiment was continued by applying deeper cuts to the existing ones to accelerate the rusting process. As previously mentioned, this salt concentration exceeds seawater's, effectively simulating harsh conditions. On day eight, rust was severe across all samples, with noticeable rust around the scratches on the pure epoxy coating. It was also observed that linseed oil-containing microcapsules performed better, as one of the samples showed no rust on the scratches except at the edges where there was no coating. In contrast, rust was more extensive around the scratches on the hemp seed oil-containing microcapsules.

In the study conducted by Behzadnasab and colleagues, where linseed oil microcapsules were incorporated into an epoxy coating, it was observed that after 6 days of salt spray testing, rust formation was significantly reduced in samples containing 10% microcapsules compared to those without microcapsules or with 5% microcapsule content [21]. In the study by Hamed Abdipour and colleagues, corrosion began within 3 days [12]. Similarly, in the Hatami Boura and colleagues' study, visible degradation was observed after 5 days [22]. This study observed no rusting in the scratches for up to 4 days, except in the epoxy coating without microcapsules. However, the 5th day of the test was not monitored, and deeper cuts were applied after the 4th day. These results indicate that the encapsulated coatings were more effective at preventing rust than coatings without microcapsules. The layer of dried oil isolates the metal substrate from direct contact with the environment, thereby protecting it from corrosion.

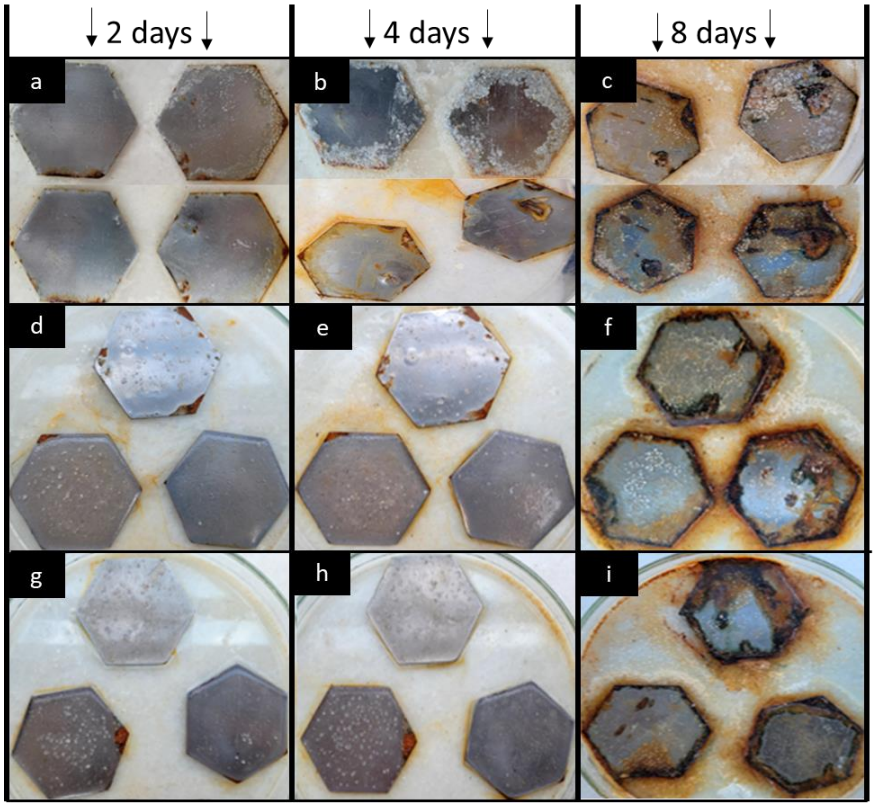

Figure 14. Salt test of (a) pure epoxy, (b) linseed oil, (c) hemp seed oil-loaded microcapsules monitored for 8 days

4. Conclusion

In this study, to prevent metal surfaces from oxidation, natural oils such as linseed and hemp seed oils were encapsulated in UF microcapsules and incorporated into an epoxy matrix as self-healing agents, providing a more sustainable approach for coated metal surfaces. The effect of stirring rate during microcapsule synthesis

is investigated by structural, morphological, thermal, particle size, and oil content analyses. Optimum morphology, particle size, and oil content were achieved at 300 rpm. The prepared microcapsules effectively slowed the oxidation of metal surfaces under harsh conditions through their self-healing mechanism, consistent with findings from previous literature. Additionally, linseed oil-containing microcapsules outperformed those containing hemp seed oil compared to the pure coating.

For further improvements, the microcapsule content in the epoxy coating can be increased (up to 30%) to enhance self-healing performance without compromising the mechanical properties of the coating. While being more sustainable, as these materials are low in cost, readily accessible, abundant, and highly effective, they will be well-suited for industrial applications.

Author Contributions

The first author conceptualized the study and supervised the findings. The second author performed the experiments. The first and second authors wrote and visualized the manuscript. The first author reviewed and edited the paper. All authors read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

Ethical Review and Approval

No approval from the Board of Ethics is required.

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