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Encapsulation of Walnut Oil in Urea-Formaldehyde for Self-Healing Coating: Effect of Mixing Speed

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Abstract

Self-healing coating is a technology where repairation of a coating can be done automatically. The self-healing agent is encapsulated in the form of microcapsules. When the microcapsules or shell material breaks, the healing agent released onto the damaged surface. In this study, walnut oil was used as a healing agent because it belongs to the drying oil which has been widely used as a coating. The polymer used as the microcapsule shell is urea-formaldehyde. This research was conducted to examine the effect of mixing speed on the diameter and thermal stability of microcapsules encapsulated by walnut oil in urea formaldehyde, as well as to see the self-healing performance. The results of FTIR testing proved that the microcapsules consist of Poly Urea Formaldehyde (PUF) as a shell material. The research showed that the mixing speed of 860 rpm produced microcapsules with the smallest diameter of 90.1426 micrometer and the highest decomposition temperature of 362.38°C. The results of self-healing tests on steel plates prove that the healing agent used has succeeded in repairing the damage by covering the surface of the scratched sample.

Keywords : encapsulation, self-healing coating, urea-formaldehid, walnut oil, mixing speed

INTRODUCTION

Environmental factors such as ultraviolet light, chemicals, and humidity have an effect on metal cracking. Self-healing coating can be a solution for this problem. Self-healing coating repairs cracks automatically without human intervention. The main elements in microcapsule-based self-healing coatings are the core and shell material. The core material functions as a healing agent in solid, liquid or gas form, while the shell material is the outer layer that protects the core material (Mishra, 2008). In self-healing coatings, microencapsulation is a common technique. Microencapsulation is a technique used to coat a core material with a polymer coating/shell material so that it becomes small, micro-sized particles (Makhlouf, 2014).

Poly Urea Formaldehyde (PUF) has been widely used as a microcapsule shell material (Gaudin & Sintes-Zydowicz, 2012), (Kosarli et al., 2019), (Tzavidi et al., 2020) because it has high mechanical strength, good chemical resistance, and low cost. The PUF shell is fragile enough to break and release the self-healing agent, but is strong enough to remain intact during the coating application process (Ollier et al., 2016).

Core materials that have been studied for their use in self-healing coatings include isocyanate (Huang & Yang, 2014), epoxy resin (Yuan et al., 2006), organic silane (Huang et al., 2012), and drying oil (Yuan et al., 2006), (Suryanarayana et al., 2008), (Mirabedini et al., 2012). Among all of these materials, drying oil has been researched the most because it is cost-effective and environmentally friendly (Wang & Zhou, 2018).

One drying oil that has not been widely studied is walnut oil. Walnut oil is one of the oils that has long been used in paints and oil paints (Stuart, 2008). Walnut oil has a high linoleic acid content of around 40-70% (Bai et al., 2017). This value is quite high when compared to linseed oil and tung oil. Linseed oil and tung oil have about 16% and 4% of linoleic acid (Oyman et al., 2005). The C=C bonds will react with oxygen in the air to form a cross-linked film (Jones, Frank N., Nichols, Mark E., Pappas, 2017). A high concentration of linoleic fatty esters guarantees the oil layer dries uniformly, whereas a high concentration of linolenic fatty esters dries quickly only on the surface and leaves unreacted fatty esters underneath (Orlova et al., 2021).

In self-healing coating applications, the diameter of microcapsules is very important because microcapsules must have good distribution in various thin coating formulations for more efficient self-healing performance (Nesterova et al., 2012). The diameter of the microcapsules can be controlled by changing the surfactant composition, the ratio of urea to formaldehyde, and the mixing speed. Research that studies the effect of surfactant on the encapsulation of walnut oil in urea formaldehyde has been done (Suyatmo, Reviana Inda Dwi; Topandi, Abdussalam; Sari, Lathiefah Oktriananda; Nulhakim, 2023).

In the encapsulation process, the mixing speed will affect the diameter and thermal stability of the resulting microcapsules. As the mixing speed increases, the diameter of the microcapsules will become smaller (Kosarli et al., 2019), (Bolimowski et al., 2018) and the thermal stability of the resulting microcapsules will also be higher. Microcapsules with a diameter of <50 μm have better self-healing coating efficiency than microcapsules with a diameter of >50 μm (Nesterova et al., 2012).

Based on the previous data, research on self-healing coatings with walnut oil as core has never been carried out so this research was conducted to determine the effect of mixing speed on this self-healing coating.

METHODS

The equipment used in this research was a three-neck flask with overhead stirrer, Eppendorf® brand 5804 centrifuge, and film applicator. Characterization of microcapsules used thermogravimetric analyzer (TGA), Fourier transform infrared (FTIR), and industrial microscope digital camera koppace.

The materials used in this research include urea from Kanto Chemical Co., Inc., formaldehyde from Merck KgaA, walnut oil from Spain, resorcinol from Merck KgaA, ammonium chloride from Merck KgaA. , polyvinyl alcohol (PVA) technical type produced by Inner Mongolia Shuangxin, distilled water, epoxy resin, and hardener.

130 ml of distilled water was mixed with polyvinyl alcohol (5%) in a three-neck flask at a reaction temperature of 55 ºC with a speed of 560 rpm, mixing for 10 minutes. Then urea (5 g), resorcinol (0,5 g), and ammonium chloride (0,5 g) were added to a three-neck flask, mixing for 15 minutes. Next, walnut oil (20 ml) was added into the three-neck flask and stirred for 15 minutes. Finally, formaldehyde (14 ml) was added to a three-neck flask and stir for 150 minutes. The encapsulation result was separated using centrifugation for 20 minutes at 4000 rpm. After centrifugation, 3 layers were obtained, the top layer was microcapsules (urea formaldehyde which had been encapsulated in walnut oil), the middle layer was the solvent or distilled water, and the bottom layer was the remaining urea-formaldehyde. The microcapsules were then separated using filter paper, rinsed using distilled water until the pH was neutral, then dried at room temperature. The same method was also used for mixing speeds of 710 rpm and 860 rpm. The dried microcapsules were then tested for diameter size using a microscope, tested for functional groups using FTIR, and tested for thermal stability using TGA.

For self-healing testing, microcapsules were mixed with epoxy resin and hardener, then stirred slowly. After that, the mixture is applied to the surface of the steel plate using a film applicator. The specimens were stored at room temperature for 6 hours then post-cured for 1 hour at 80°C. A scratch was made 1 cm long and left for 5 days at room temperature, then thermal curing was carried out at 80°C for 4 hours. The sample was then viewed using a microscope.

RESULTS AND DISCUSSION

Urea-formaldehyde microcapsules encapsulated with walnut oil were then tested for their functional groups, diameter, and thermal stability. These microcapsules were then also tested for their self-healing performance by mixing them in epoxy resin which was then applied as a coating on a steel plate.

FTIR

FTIR was used to see the success of the encapsulation process of walnut oil in urea-formaldehyde based on the functional groups produced. Based on the FTIR test results in Figure 1, PUF characteristics occur at wave numbers 2900 cm^{-1} and 2800 cm^{-1} which indicate the C-H group, wave numbers 1700 cm^{-1} indicate the C=O group, wave numbers 1600 cm^{-1} indicate the N-H group, and a wave of 1500 cm^{-1} indicate a C-N group. The results of functional group testing showed that the microcapsules formed a PUF shell as in previous research (Shahabudin et al., 2016), (Kurt Çömlekçi & Ulutan, 2018).

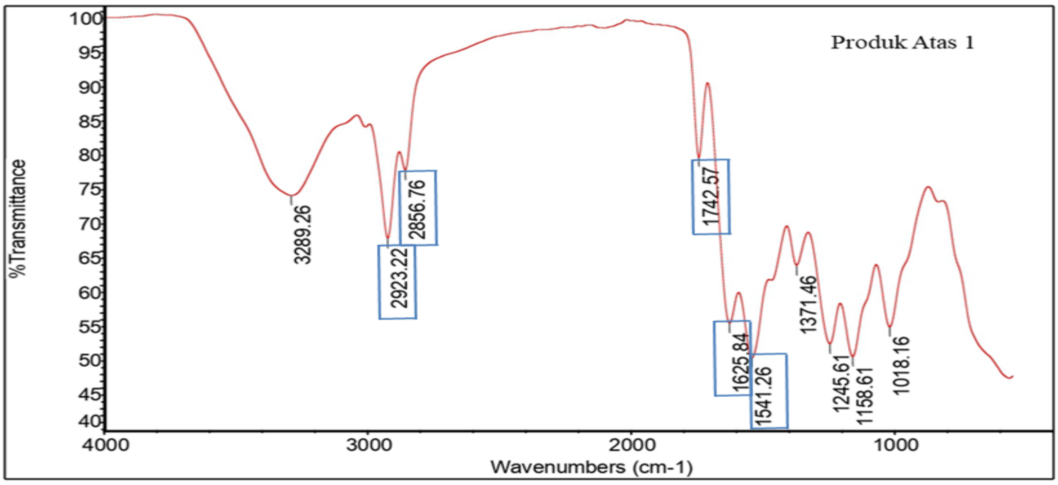


Figure 1. Microcapsule FTIR Result

Diameter of Microcapsules

The results of the average diameter of microcapsules can be seen ini Table 1. It showed that there was an influence of mixing speed on the average diameter of microcapsules from encapsulation of walnut oil in urea formaldehyde. A mixing speed of 860 rpm has a smaller average diameter of microcapsules, 90.1426 µm. The decrease in the average diameter of microcapsules is in accordance with previous research (Kosarli et al., 2019) which stated that encapsulation with a mixing speed of 800 rpm produced a smaller diameter of microcapsules, 64 ± 27.6 µm. However, to obtain better self-healing performance, it is necessary to optimize the microcapsule diameter size of <50 µm which can be produced with a higher mixing speed or changing the mass ratio of urea and formaldehyde used, and the pH during the encapsulation process (Nesterova et al., 2012).

Table 1. Microcapsule Average Diameter

Mixing Speed, rpm	Average Diameter, µm
560	192,4647
710	139,5830
860	90,1426

Thermal Stability

Thermal stability testing uses a Thermogravimetric Analyzer (TGA) TA 55 and standard E 1131-08. The sample used was 15-16 mg. The operating temperature range used is 50°C to 800°C. The decomposition of microcapsules can be seen in Figure 2,3, and 4 also in Table 2. Microcapsules with a mixing speed of 560 rpm began to decompose at a temperature of 345.57°C. Microcapsules with a mixing speed of 710 rpm began to decompose at a temperature of 359.87°C and microcapsules with a mixing speed of 860 rpm began to decompose at a temperature of 362.38°C. This data shows that a higher mixing speed can increase thermal stability. At a temperature of around 50°C-130°C, microcapsule loses volatile substances such as formaldehyde and moisture content (water). At a temperature of around 360°C-430°C it loses PUF shell compounds and walnut oil and then around

430°C-800°C decomposes completely. This result is in accordance with previous research where higher mixing speeds produce high thermal stability (Kosarli et al., 2019). Based on this result, it matches with previous research (Kurt Çömlekçi & Ulutan, 2018) which states that microcapsules must have thermal stability around 120°C in accordance with thermal applications in the coating industry.

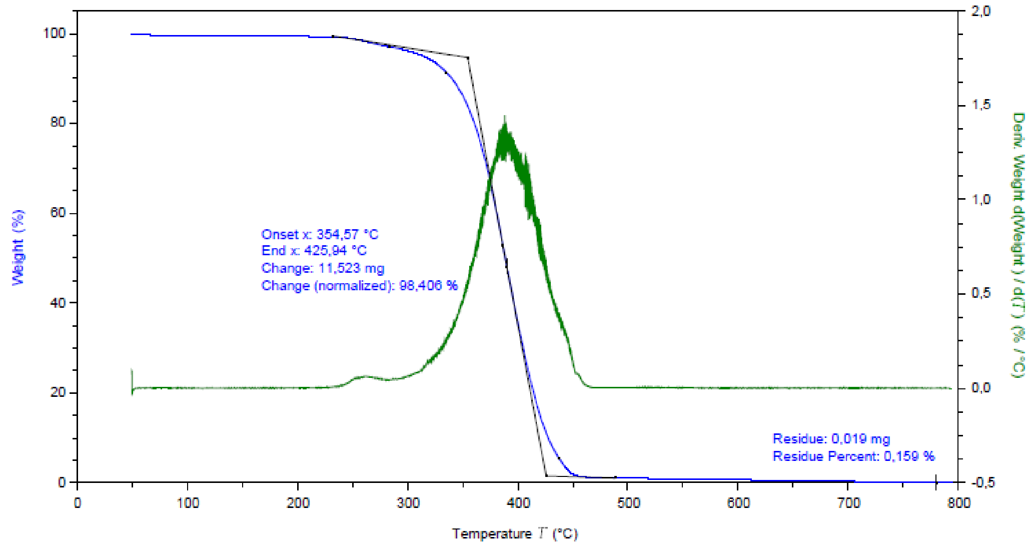


Figure 2. Graph of Thermal Stability Microcapsule with Mixing Speed of 560 rpm

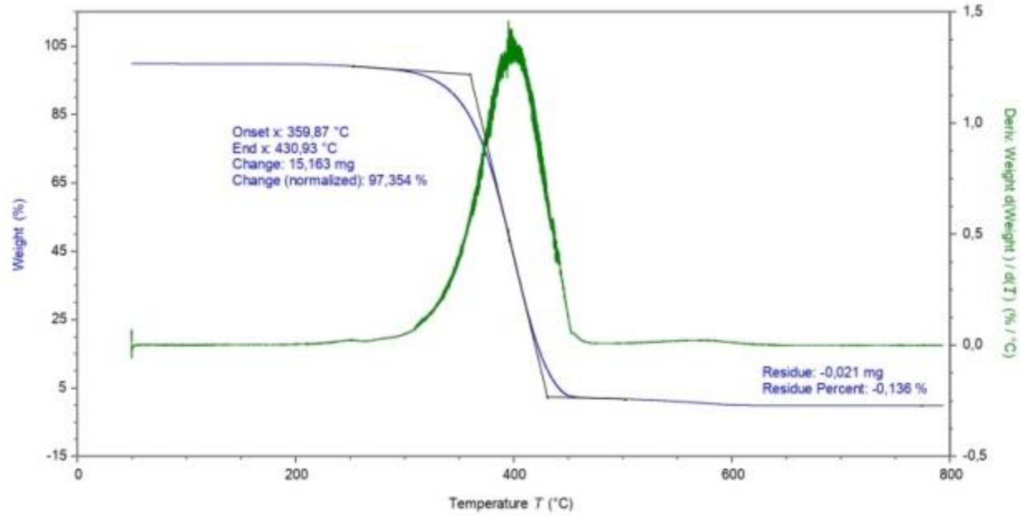


Figure 3. Graph of Thermal Stability Microcapsule with Mixing Speed of 710 rpm

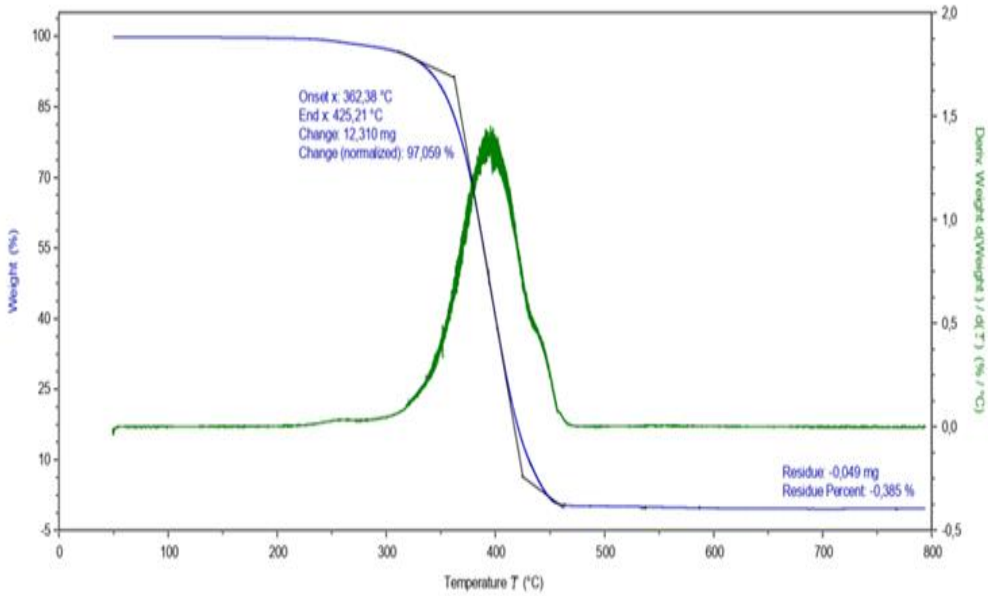


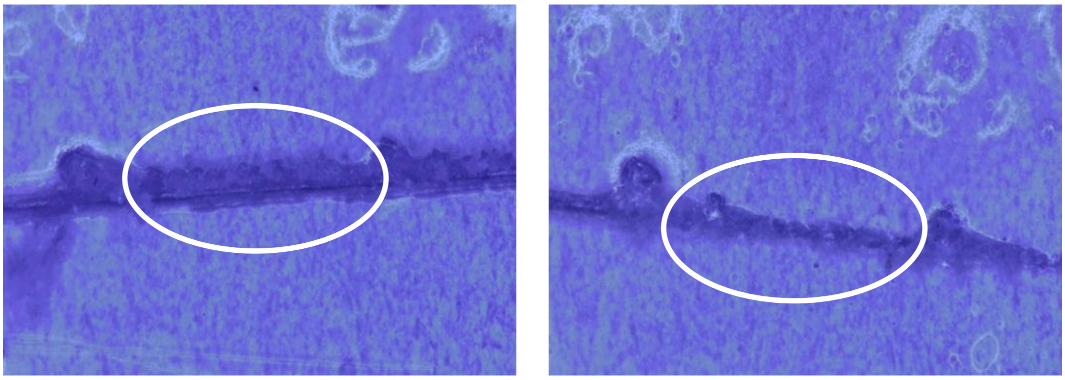
Figure 4. Graph of Thermal Stability Microcapsule with Mixing Speed of 860 rpm

Table 2. Thermal Stability of Microcapsules

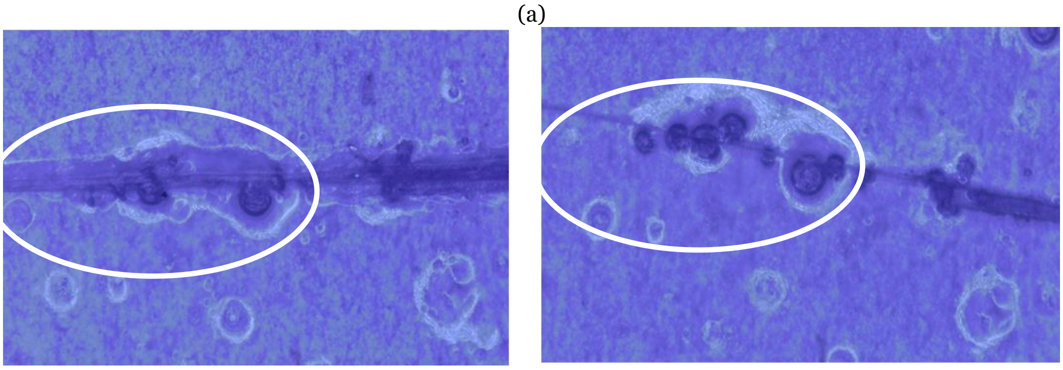
Mixing Speed, rpm	Tonset (°C)	Tendset (°C)
560 rpm	345,57°C	425,94°C
710 rpm	359,87°C	430,93°C
860 rpm	362,38°C	425,21°C

Self-Healing

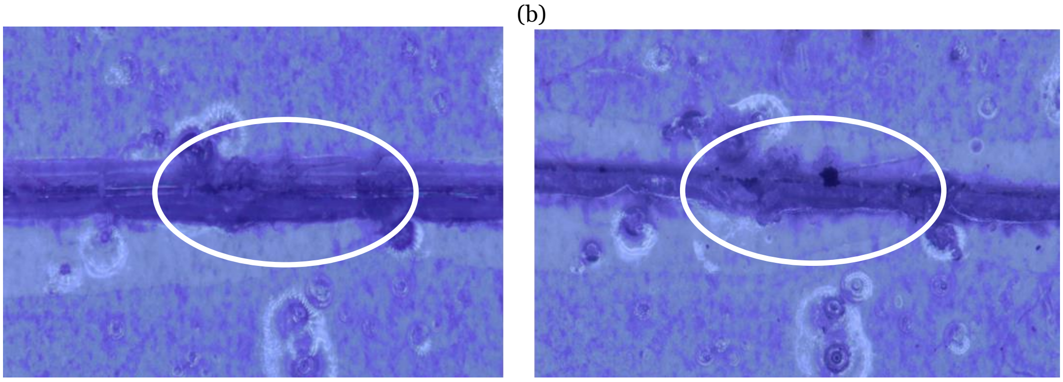
The results of self-healing tests on steel plates which can be seen in Figure 5. It can be seen that in the part circled in white, the coating that was left for 5 days has a smaller width than the coating straight after scratching. This indicates that after the microcapsules broke due to scratch, the self-healing agent which is walnut oil was then released and covered the damaged surface scratches. After that, the walnut oil polymerizes in the presence of oxygen in the air to form a protective layer or film.. As shown in Figure 5, walnut oil as self-healing agents are able to cover surfaces that are scratched or damaged due to the external environment. The results of self-healing tests on steel plates are in accordance with another research conducted by Abdipour et al. (2018). However, to obtain better self-healing performance, it is necessary to optimize the diameter of the microcapsules <50 μm which can be obtained by changing mixing speed, type of stirrer, the mass ratio of urea and formaldehyde used, and the pH during the encapsulation process.



(a)



(b)



(c)

Figure 5. Self-Healing Test of Microcapsules on Plate Steel (a) 560 rpm, (b) 710 rpm, dan (c) 860 rpm. (left : straight after scratching and right : 5 days after scratching)

CONCLUSION

Based on the results of research data analysis, it can be concluded that the PUF shell was successfully formed in the microencapsulation process and the mixing speed influenced the average diameter size and thermal stability of the resulting microcapsules. The higher the mixing speed used, the smaller the diameter of the microcapsules produced and the higher the thermal stability. Testing of the self-healing performance resulting from encapsulation of walnut oil in urea formaldehyde on a steel plate proved that the resulting microcapsules could repair damage by covering the scratches that had been made. To get microcapsules with a smaller diameter, it is necessary to use a higher mixing speed and look at other factors such as the addition of surfactant and the ratio of urea to formaldehyde.

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