Preparation and application of polysulfone microcapsules containing tung oil in self-healing and self-lubricating epoxy coating

Haiyan Li, Yexiang Cui, Huaiyuan Wang*, Yanji Zhu, Baohui Wang

Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, PR China

Corresponding author：Huaiyuan Wang, Email: wanghyjiji@163.com, Tel.:86-459-6503083

Abstract：Polysulfone microcapsules containing tung oil were synthesized by a solvent evaporation method. The mean diameter and wall thickness of the synthesized microcapsules were approximately 130 μm and 9 μm, respectively. High thermal stability of the microcapsules with a thermal degradation onset temperature of 350°C was obtained. The multi-functional coating was fabricated by incorporating the microcapsules containing tung oil into an epoxy matrix. The self-healing and self-lubricating functions were evaluated by corrosion and tribology test. 10 wt% microcapsules embedded in epoxy coating offered optimum results. The microcapsules showed excellent anticorrosion performance in scratched coatings, which was attributed to the formation of a cross-linked polymer film after tung oil was released from the damaged microcapsules. The frictional coefficient and wear rate of the self-lubricating coating decreased significantly as compared to the neat epoxy. The formation of a transfer film from releasing tung oil and the entrapment of wear particles in the cavities left by the ruptured microcapsules were the major antifriction mechanism.

Keywords: Tung oil; PSF microcapsules; self-healing; self-lubricating; coating

1. Introduction

Self-healing coatings have drawn great attention in recent years due to their ability to heal damage automatically. The self-healing function of coatings can be achieved vis embedding microcapsules, nanocontainers[1–3] into a matrix or by reconstructing intrinsic dynamic chemical bonds in the molecular structures[4–6]. Corrosion protective self-healing coatings based on microcapsules have been investigated intensively. Several corrosion-protective agents have been microencapsulated and then added into a matrix to prepare self-healing corrosion coatings. Reactive chemicals such as dicyclopentadiene(DCPD)[7], epoxy[8,9], isophorone diisocyanate(IPDI)[10], hexamethylene diisocyanate (HDI)[11], cinnamide moiety-containing polydimethylsiloxane (CA-PDMS), and hydrolysable organic silane[12,13] have been released from microcapsules when damage occurred and subsequently polymerized in the presence of catalyst. The cross-linked polymer film was formed automatically to retard corrosion. Corrosion inhibitors are an effective corrosion-protective agent. They have been microencapsulated successfully for self-healing coatings[14,15]. However, the high environmental toxicity of these coatings has restricted their application in many countries. Drying oil is a kind of environmentally friendly corrosion-protective agent. Linseed oil, a widely used drying oil, has been microencapsulated by using poly(urea-formaldehyde) (PUF) or ethylcellulose as wall materials[16–21]. When the drying oil is released from damaged microcapsules and comes into contact with oxygen, polymerization occurs and a corrosion-slowing film is formed.

The fabrication of self-lubricating materials by incorporating lubricant-loaded microcapsules into a matrix has been reported widely. In the system of self-lubricating materials, a liquid lubricant is released to the surface as the solid matrix wears out, without the need for external intervention or maintenance. This significantly decreases friction coefficients. Many relevant studies have been reported aimed at bulk polymer. Paraffin wax[22–25], lubricant oil[26–28], sulfureted fatty[29], and hexamethylene disocyanate (HDI)[30] have been microencapsulated and incorporated into bulk polymers to prepared self-lubricating materials. The tribological tests showed effective reductions in friction coefficients and wear rates. Although there are few reports about polymer-based self-lubricating coatings, Bandeira and co-workers studied the incorporation of microcapsules containing an ionic liquid lubricant in polytetrafluoroethylene (PTFE) coatings. The tribology properties were evaluated[31].

Armada et al. incorporated lubricant-loaded microcapsules into a nylon matrix by a thermal spray process. The self-lubricating properties of coatings have been investigated[32]. Yang et al. prepared a polyurethane self-lubricating coating by adding silica gel shell microcapsules containing an ionic liquid. The coating displayed a much lower friction coefficient and less wear as compared to a coating with unfilled microcapsules[33].

It is a new concept to fabricate a multi-function coating that has dual self-healing and self-lubricating functions. In this study, a multi-function coating was developed by incorporating polysulfone (PSF) microcapsules containing tung oil. Tung oil, which is a drying oil, has some properties similar to linseed oil. The main constituent is a glyceride of an elaeostearic acid, a conjugated triene. This highly unsaturated and conjugated system is largely responsible for the rapid polymerization. The cross linking of the tung oil's molecules makes the surface waterproof and impermeable to many chemicals. Tung oil is widely used in paints, waterproof coating, varnishes. As tung oil dries and cures, the molecules join together in a tight complex formation, the bonding also gives flexibility to the surface, making it capable of withstanding wear and tear[21]. Tung oil has excellent thermal stability and viscosity, similar to lubricant oil, which give it a lubricating effect and helps minimizes corrosion. Therefore, tung oil can be considered as self-healing agent and self-lubricant. PSF was chosen as the wall material of the microcapsules because it has high chemical and physical stability, excellent thermal stability, and high mechanical strength[34, 35]. The self-healing performance was characterized by corrosion test. The self-lubricating property was evaluated by tribological test.

2. Experimental

2.1 Materials

Tung oil was supplied by Guangzhou hanhao Chemical Co. Ltd. (China). PSF was purchased from Dalian PSF Technology Co. Ltd (China). Dichloromethane (DCM, >99.5wt%) and Polyvinyl alcohol(PVA) (degree of polymerization = 1750±50) were purchased from Tianjin Damao Co.(China). Gelatin (> 99wt%) was obtained from Tianjin Zhiyuan Chemical Reagents Co. Ltd (China). Bisphenol-A epoxy resin (type E51) and tetraethylenepentamine(TEPA) curing agent were supplied by Heilongjiang chemical Engineering Institute Co. Ltd.(China). Deionized water was used throughout the study. All materials were used as received without any further purification.

2.2 Synthesis of PSF microcapsules containing tung oil

Tung oil-loaded PSF microcapsules were prepared by the solvent evaporation method. The encapsulate mechanism is shown in Figure 1. Tung oil (1.2 g) and PSF (1.0 g) were mixed with 20 mL of DCM. Then the mixture was added dropwise to 50 mL of a mixed of 0.8 wt% gelatin and 1.0 wt% PVA with mechanical stirring at 700 rpm. After reacting for 2 h at 37℃, the DCM evaporated completely and PSF microcapsules containing tung oil were obtained. The synthetic microcapsules were collected by filtration, washed several times with deionized water, and finally dried.

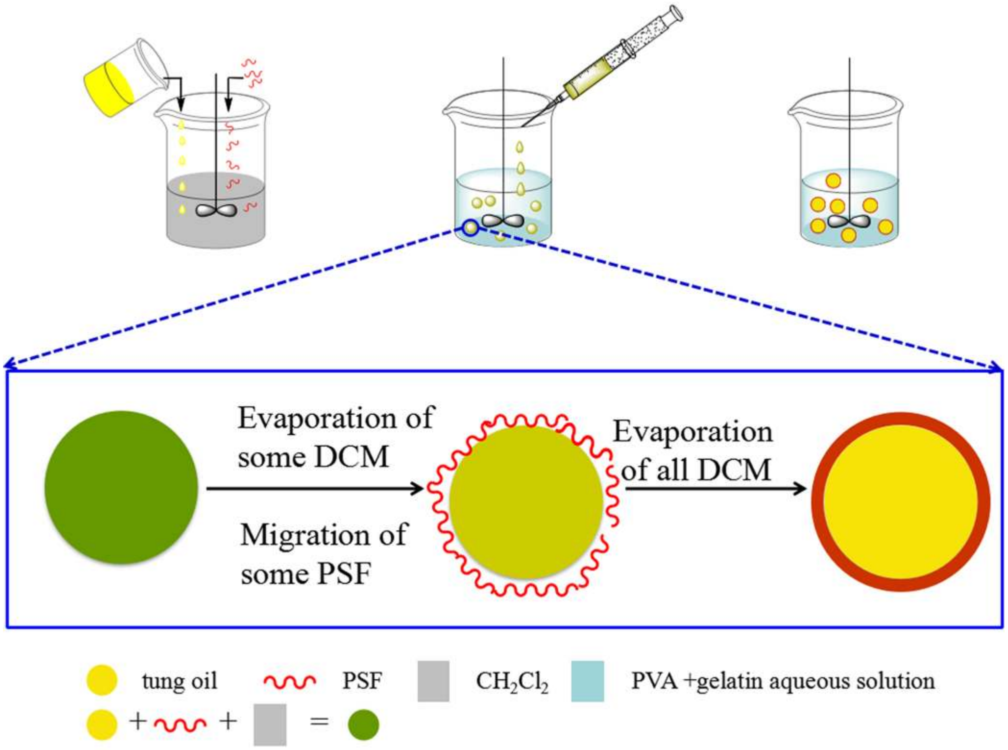

Figure 1 The schematic of microencapsulation mechanism

2.3 Preparation of multi-functional coatings

Epoxy-based multi-functional coatings were manufactured by mixing the preheated (60°C) epoxy with a 12wt% TEPA curing agent. Then, the 10wt% microcapsules were added into the mixture in batches with stirring for 10 min. After ultrasonic agitation for 10 min, the bubbles were removed in a vacuum drying oven. Steel plates (size, 80 ×80×1 mm^3) were polished with sand paper, degreased with acetone, and finally washed with distilled water. Each dried steel plate was coated with the epoxy mixture to a layer thickness of approximately 200 μm, cured for 3 h at room temperature and then 80°C for 6 h. Control samples were coated by an epoxy system without microcapsules and with the same thickness.

2.4 Characterizations

Infrared spectra (FTIR) was employed to analyze the chemical structure of microcapsules in the wavenumber range from 4000 cm^{-1} to 500 cm^{-1}. The thermal stability of the PSF microcapsules containing tung oil was evaluated using thermogravimetric analysis (TGA). Measurements were carried out over a 25–800°C temperature range at a heating rate of 10°C/min under N_2 atmosphere. The morphology of the microcapsules and the wear surface of coating were observed using scanning electron microscopy (SEM). The microcapsules and wear surface of the coating samples were coated with a gold layer by sputtering to promote a metallic conductive surface for improved SEM observation. The diameters of the microcapsules were measured using an optical microscope, and the particle-size distribution was measured in data sets of at least 200 measurements.

The self-healing performance of the coatings was evaluated by corrosion test. Cross scratches were applied manually using a razor blade on the prepared epoxy-based coatings and then the coatings were given 24 h to heal themselves. The scratched coatings were immersed in a 10wt% NaCl solution for 1, 4 and 7d to allow for corrosion.

The self-lubricating performance of the coatings was evaluated by friction and wear tests. The tests were conducted on a friction and wear tester with a pin-on-disc configuration in the normal sliding direction. A schematic diagram of the friction and wear tests are presented in Figure 2. The applied load was 1.0 MPa and the sliding velocities was 0.51 m/s. The friction duration was 50 min. The friction coefficient and wear rate were calculated by the equation given in our previous study[36]. Before each test, the surfaces of stainless steel counterpart ring and specimen were polished with 1000-grit paper to an average roughness of 0.15–0.3 μm and then cleaned with anhydrous ethanol. All tests were conducted under ambient laboratory conditions. Three measurements per sample were taken to get the mean and standard deviation.

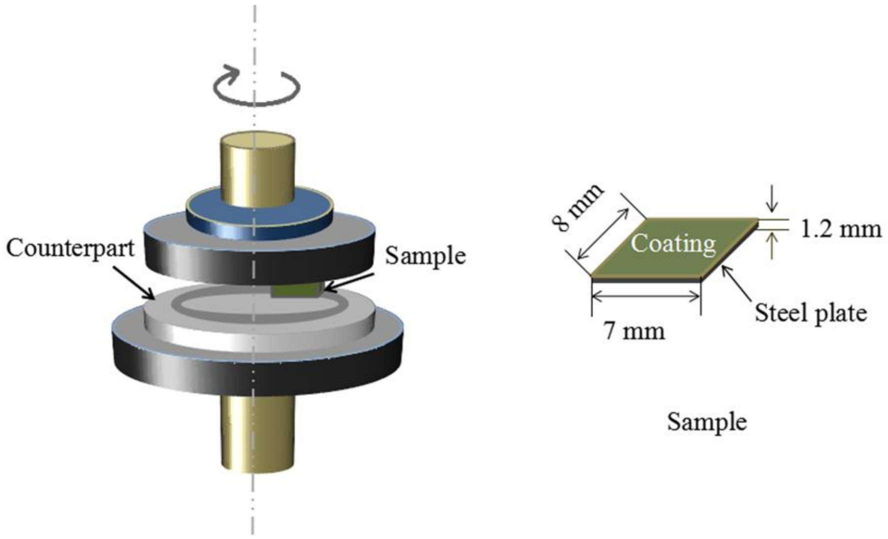

Figure 2 Schematic diagram of the friction and wear tests

3. Results and discussion

Figure 3(a) shows the SEM micrographs of tung oil-loaded microcapsules. Figure 3(b) shows the SEM micrograph of a single microcapsule at high magnification. The synthetic microcapsules presented regular, compact, and spherical structures with smooth outside surfaces. Figure 3(c) shows the SEM micrograph of a ruptured microcapsule with a uniform shell wall thickness of approximately 9 μm. Figure 3(d) shows the particle-size distribution of the microcapsules, the average diameter of the particles was approximately 130 μm.

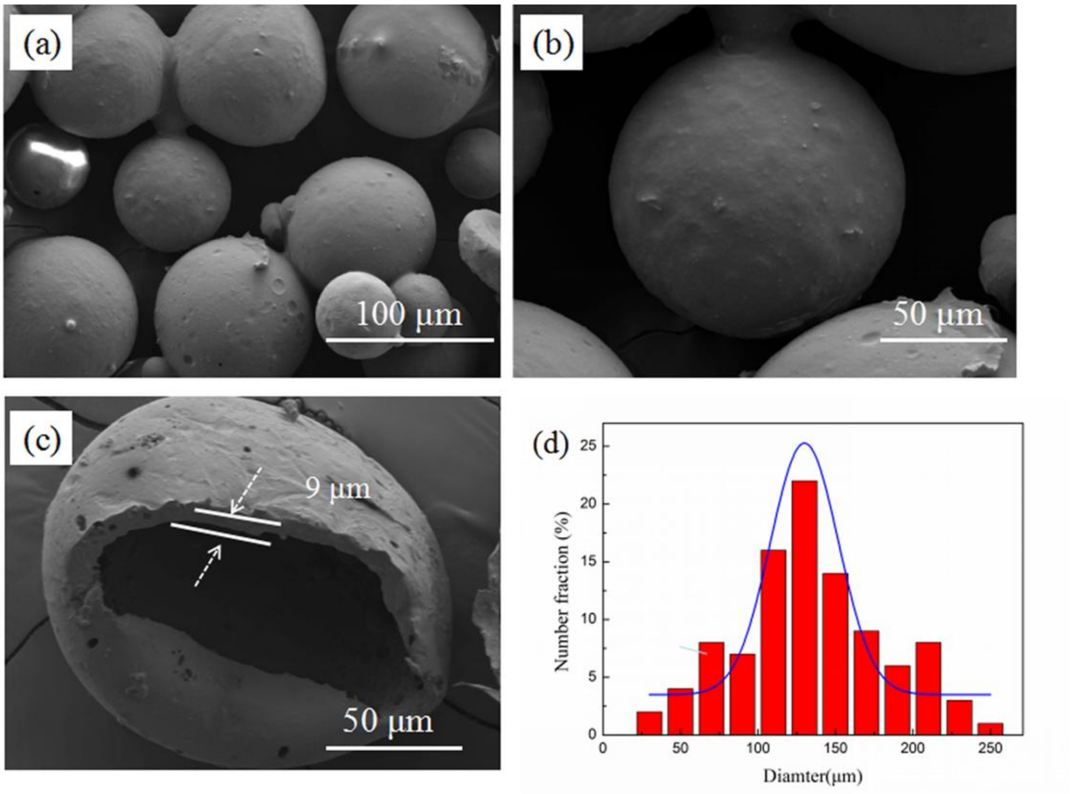

Figure 3 SEM micrographs and size distribution of tung oil-loaded microcapsules (a) microcapsules magnification：100× (b) microcapsules magnification：200× (c) ruptured microcapsule (d) size distribution

Figure 4 shows the FTIR spectra of the tung oil-loaded microcapsules, PSF and tung oil. Microcapsules spectra shows characteristic peeks of PSF at: ~1488 and ~1587 cm^{-1} (C=C aromatic rings stretching vibration), ~1322 and ~1294 cm^{-1}(O=S=O asymmetric stretching vibration), ~1239 cm^{-1} (C-O-C stretching vibration)[37]. The spectrum of microcapsules also shown the characteristic peeks of tung oil at: ~3012 cm^{-1} (=C–H stretching vibration), ~2927 and ~2855 cm^{-1}(–C–H stretching vibration), ~1745 cm^{-1}(C=O stretching vibration), ~725 cm^{-1} ($-(CH_2)_n-$ ($n \geqslant 4$) bending vibration), FTIR curves confirm encapsulation of tung oil in the PSF particles.

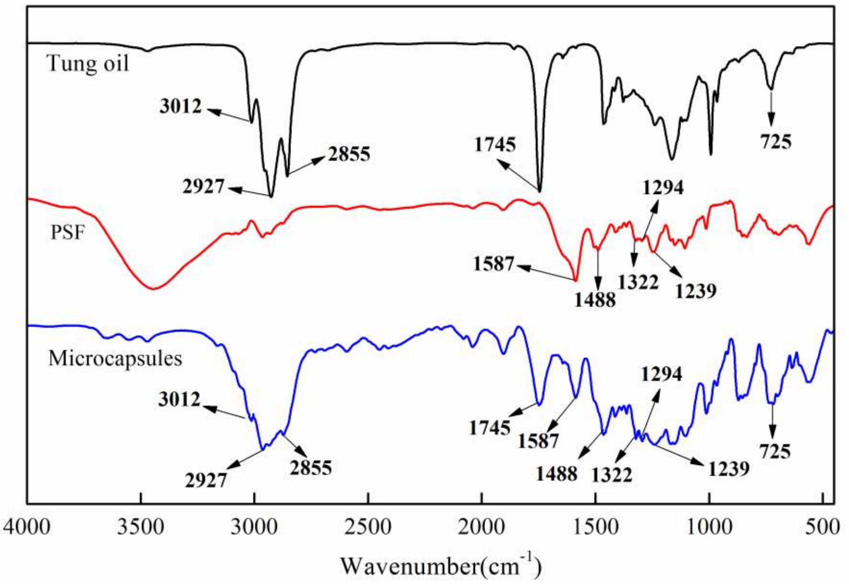

Figure 4 FTIR spectra of microcapsules, PSF and tung oil

The thermal stability of microcapsules, pure tung oil, and PSF were analyzed and the results are shown in Figure 5. The initial decomposition temperature of PSF was 490°C, which is obviously higher than that of frequently used microcapsule wall materials such as PUF (240°C[22]), polyurea (200°C[30]) and poly(melamine-formaldehyde) (260°C[28]). The residual weight was 32 wt% at 800°C, probably due to the formation of thermally stable carbonaceous materials because of the presence of aromatic structures in the PSF polymer backbone[31]. Pure tung oil began to evaporate at 350°C, and this process was completed at 375°C. High thermal oxidative stability is an essential property for lubricants because in addition to reducing friction and wear, liquid lubricants are needed to cool the rubbing surfaces that are heated due to friction. The thermal degradation onset temperature of microcapsules was 350°C, but the slope of this curve was smaller than of tung oil, which indicates that tung oil was successfully encapsulated by PSF. The encapsulation capacity of the microcapsules was 50.1 wt%, which was calculated from the TG curve of microcapsules.

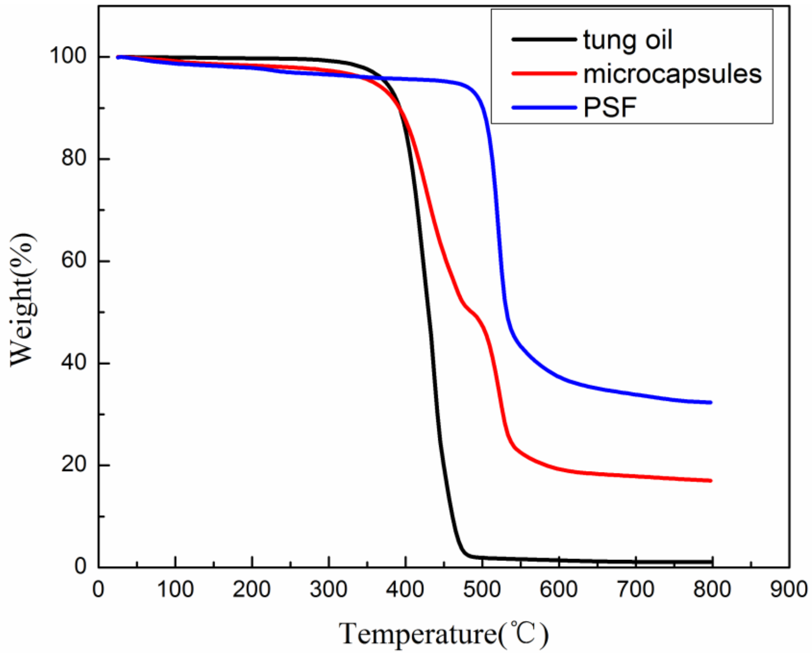

Figure 5 TGA curves of PSF, tung oil filled microcapsules and tung oil

Figure 6 shows the visual appearance of the scratched area of the coated sample after 0, 1, 4, and 7d. For the neat epoxy sample, rusting occurred along the scratched area. Increasing the immersion time, corrosion became more serious, as shown in Figure 7(a1)–(a4). For the microcapsule-filled coating, we can see from Figure 5(b1)–(b4) that corrosion was much less visible. The scratched areas of the steel plates with the self-healing coating were nearly fully free of corrosion after 1d and 4d. After 7d, there was very little rust. It was believed that in the microcapsules-filled coating, a new coating layer was formed in the scratched area upon rupture of the microcapsules and subsequent release of the core materials, i.e. tung oil. Figure 7 shows the SEM morphology of the scratched area of the control sample and a self-healing coating sample. For the control sample, a scratch can be seen clearly in Figure 7(a). For the self-healing coating sample, a new self-healing layer was observed, as shown in Figure 7(b). The newly formed self-healing layer was able to reduce the corrosion of the steel plates. The self-healing mechanism is shown in Figure 8. The tung oil released from the ruptured microcapsules can seal and heal the crack automatically by reacting with the surrounding oxygen.

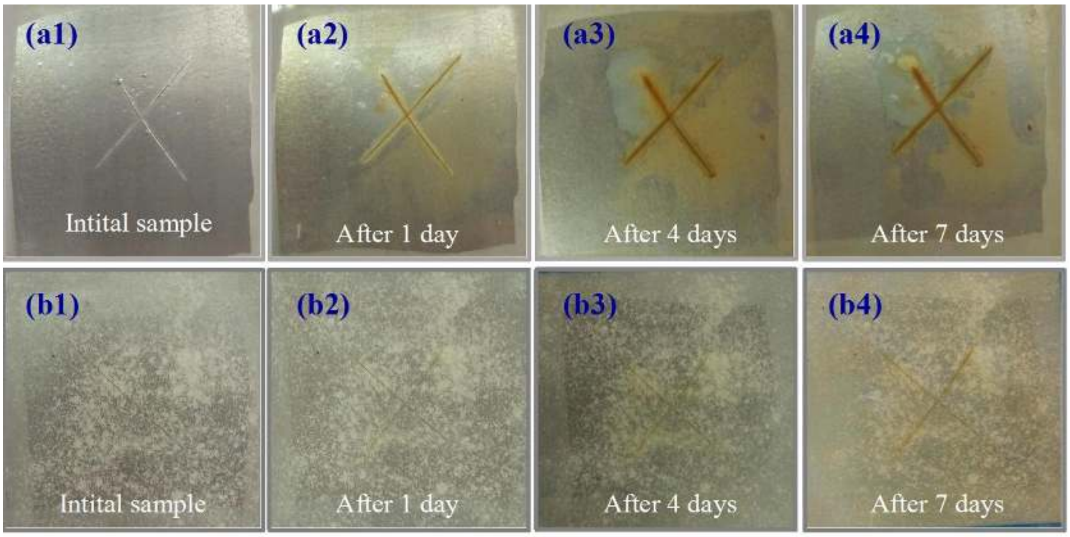

Figure 6 Optical photographs of corrosion protection of steel plates: (a1-a4) pure control epoxy scratched coating with immersion time of 0, 1, 4, 7 days, (b1-b4) self-healing epoxy scratched coating by incorporating 10 wt% microcapsules with immersion time of 0, 1, 4, 7 days

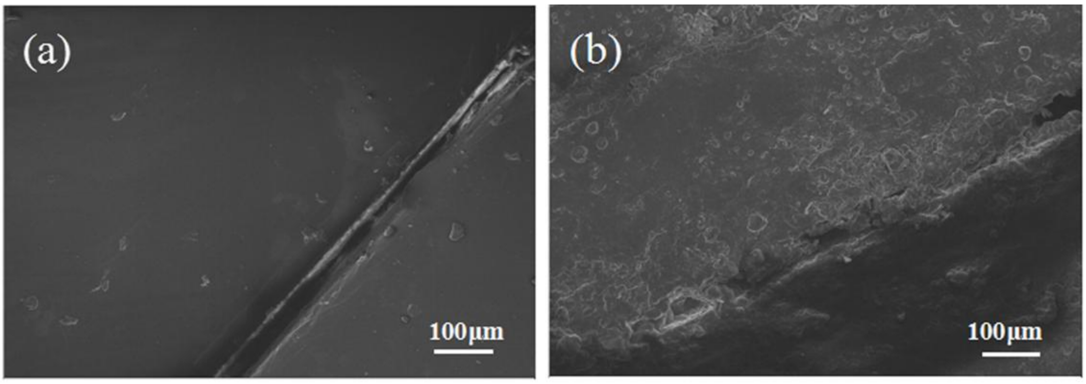

Figure 7 SEM micrographs of the scratched area of (a) control coating, (b) self-healing coating with 10 wt% microcapsules

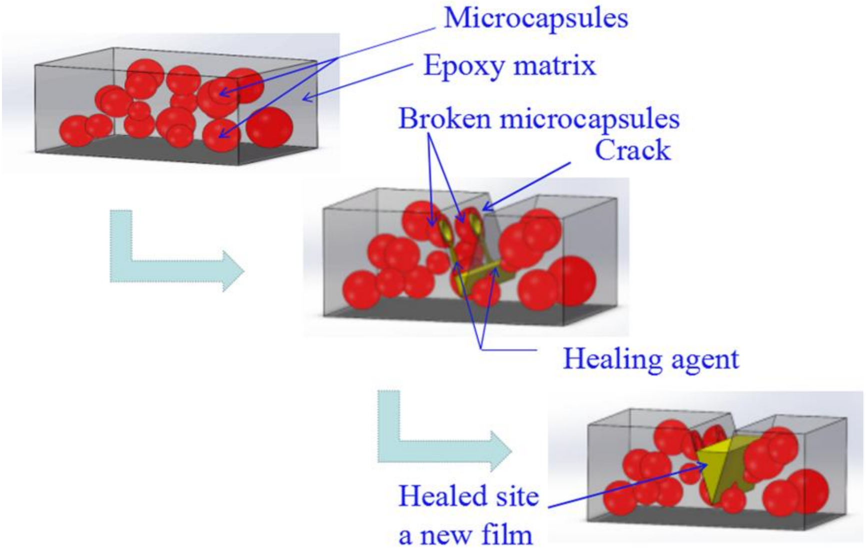

Figure 8 Schematic diagram of self-healing mechanism

The self-lubricating property of the coating was evaluated by tribology tests. Figure 9 shows the sliding wear properties of the coating. Clearly, incorporation of the tung oil-loaded microcapsules can decrease the frictional coefficient and wear rate of the coating. At a microcapsules content of 10 wt%, the lowest frictional coefficient and specific wear rate of the coating were 0.35 and 13.10×10^{-14} m^3/Nm, respectively, values that are much lower than those of unfilled epoxy, i.e. 0.46 and 38.64×10^{-14} m^3/Nm. When the microcapsule concentration was further increased to 15 wt% and then 20 wt%, the frictional coefficient and wear rate gradually increased. This phenomenon was attributed to the decreased mechanical properties with increasing microcapsule content, which were reported in our previous study[26]. The stiffness and strength of a materials is an important parameter for controlling its wear resistance[27]. Figure 10 shows the schematic diagrams of the antifriction mechanism of the self-lubricating epoxy coating. The incorporated microcapsules ruptured and released the tung oil in the progress of tribology and then formed a transfer film that reduced the friction by preventing direct contact between the steel counterpart and the epoxy coating.

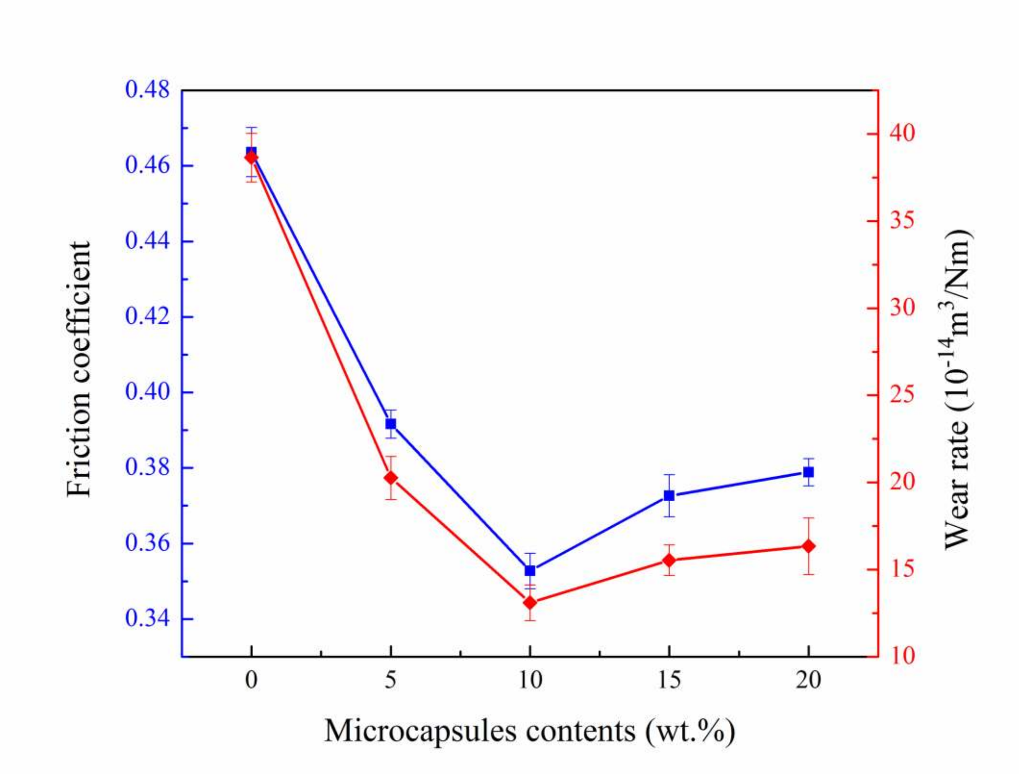

Figure 9 Frictional coefficients and specific wear rate of self-lubricant coating versus content of the Tung oil-loaded microcapsules

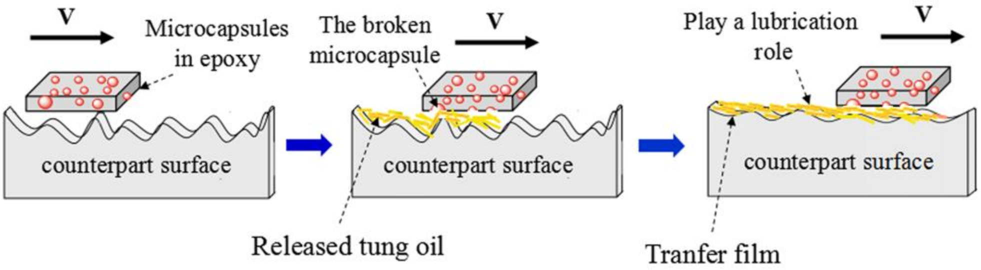

Figure 10 The schematic diagrams of antifriction mechanism of self-lubricating coating

After the tribological tests, the wear surface morphologies of the control coating and the self-lubricant coating were observed using SEM, as shown in Figure 11. Comparing Figure 11(a) and Figure 11(b), the wear morphology was rough for the control coating, which can be attributed to the surface fatigue wear. For the self-lubricant coating, the wear surface was much smoother than that of the control coating. The formation of a transfer lubricating film reduced the fatigue wear and helped to separate the contact surface.

In addition to the ability of the transfer lubricating film to decrease the frictional coefficient and wear rate, the ruptures microcapsules also trap wear debris. Cavities representing the ruptured microcapsules are clearly observed in Figure 11(b). Figure 11(c) further reveals that wear debris was trapped in the cavities of worn microcapsules. The reduction in the amount of wear debris due to entrapment via the cavities weakened the abrasive effect of the wear debris as a third body in the contact area, which also decreased the frictional coefficient and wear rate. Similar results were reported by Zhang and coworkers[28].

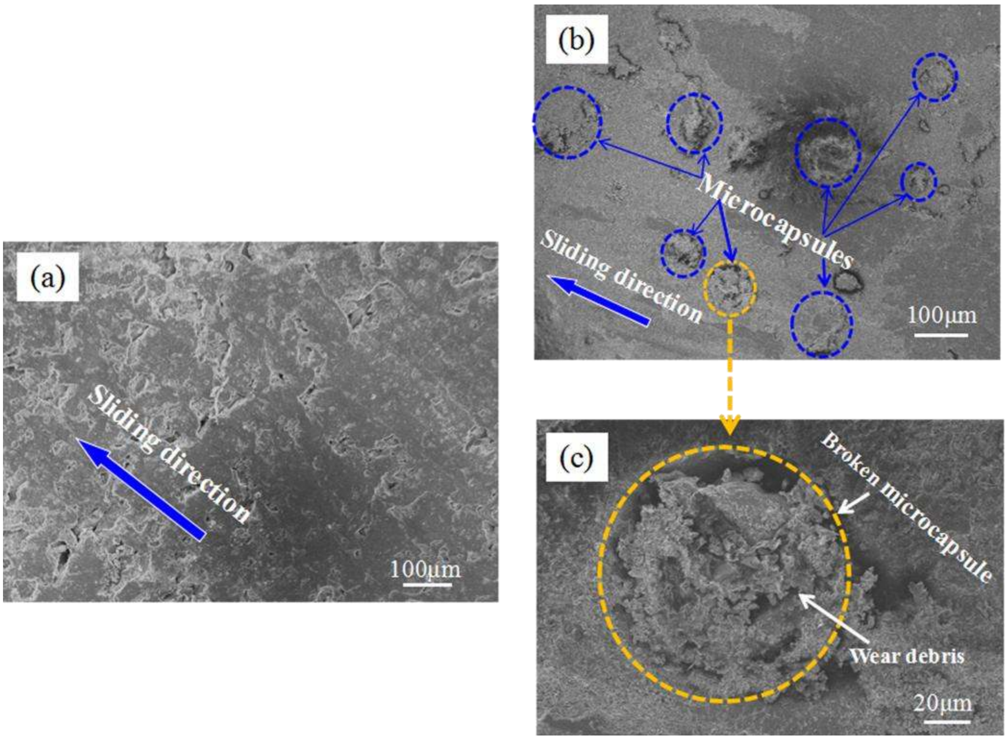

Figure 11 SEM images of the worn surface (a) control coating (b) self-lubricating coating filled with 10 wt% tung oil-loaded microcapsules (c) close view of a cavity left by the ruptured microcapsule. The arrows indicate the sliding direction.

4. Conclusions

PSF microcapsules containing tung oil were successfully prepared using a simple solvent evaporation method. The microcapsules had mean spherical dimeters of approximately 130 μm and wall thickness of approximately 9 μm. Self-healing and self-lubricating multi-functional coatings were also fabricated by adding the microcapsules into epoxy. When the concentration of microcapsules was 10 wt%, excellent corrosion-protection performance was presented, which was attributed to the self-healing function of tung oil. The wear resistance was also much improved relative to the pure epoxy coatings. A boundary transfer lubricating film formed during the tribology process contributed the self-lubricating function.

Acknowledgments: The research is financially supported by the National Young Top Talents Plan of China (2013042), National Science Foundation of China (Grant No. 51175066), Program for New Century Excellent Talents in University (NCET-12-0704), the Science Foundation for Distinguished Young Scholars of Heilongjiang Province (JC201403), and Natural Science Foundation of Heilongjiang Province (E2015034).

References

[1] D.G. Shchukin, M. Zheludkevich, K. Yasakau, S. Lamaka, M.G.S. Ferreira, H. Mohwald, Layer-by-layer assembled nanocontainers for self-healing corrosion protection, Adv. Mater. 18 (2006) 1672-1678.

[2] T. Chen, R.P. Chen, Z. Jin, J. Liu, Engineering hollow mesoporous silica nanocontainers with molecular switches for continuous self-healing anticorrosion coating, J. Mater. Chem. A. 3 (2015) 9510-9516.

[3] D, Borisova, D. Akçakayıran, M. Schenderlein, H. Mohwald, D.G. Shchukin, Nanocontainer-based anticorrosive coatings: effect of the container size on the self-healing performance, Adv. Funct. Mater. 23 (2013) 3799-3812.

[4] S. Coulibaly, A. Roulin, S. Balog, M.V. Biyani, J. Foster, S.J. Rowan, G.L. Fiore, C. Weder, Reinforcement of optically healable supramolecular polymers with cellulose nanocrystals, Macromolecules 47 (2014) 152-160.

[5] Z.H. Wang, Y. Yang, R. Burtovyy, I. Luzinov, M.W. Urban, UV-induced self-repairing polydimethylsiloxane–polyurethane (PDMS–PUR) and polyethylene glycol–polyurethane (PEG–PUR) Cu-catalyzed Network, J. Mater. Chem. A. 2 (2014) 15527-15534.

[6] G. Postiglione, S. Turri, M. Levi, Effect of the plasticizer on the self-healing properties of a polymercoating based on the thermoreversible Diels–Alder reaction, Prog. Org. Coat. 78 (2015) 526-531.

[7] S.R White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, S. Viswanathan, Autonomic healing of polymer composite, Nature 409

(2001) 794-797.

[8] X.X. Liu, H.R. Zhang, J.X. Wang, Z. Wang, S.H. Wang, Preparation of epoxy microcapsule based self-healing coatings and their behavior, Surf. Coat. Tech. 206 (2012) 4976-4980.

[9] L.P. Liao, W. Zhang, Y. Zhao, Preparation and healing property evaluation of self-repairing polymer coating, Surf. Eng. 30 (2014) 138-141.

[10] W. Wang, L.K. Xu, X.B. Li, Y. Yang, E.P. An, Self-healing properties of protective coatings containing isophorone diisocyanate microcapsules on carbon steel surfaces, Corros. Sci. 80 (2014) 528-535.

[11] D.W. Sun, J.L. An, G. Wu, J.L. Yang, Double-layered reactive microcapsules with excellent thermal and non-polar solvent resistance for self-healing coatings, J. Mater. Chem. A. 3 (2015) 4435-4444.

[12] Y.K. Song, C.M. Chung, Repeatable self-healing of a microcapsule-type protective coating, Polym. Chem. 4 (2013) 4940-4947.

[13] M.X. Huang, H. Zhang, J.L. Yang, Synthesis of organic silane microcapsules for self-healing corrosion resistant polymer coatings, Corros. Sci. 65 (2012) 561-566.

[14] A. Kumar, L.D. Stephenson, J.N. Murray, Self-healing coatings for steel, Prog. Org. Coat. 55 (2006) 244-253.

[15] N.K. Mehta, M.N. Bogere, Environmental studies of smart/self-healing coating system for steel, Prog. Org. Coat. 64 (2009) 419-428.

[16] C. Suryanarayan, K.C. Rao, D. Kumar, Preparation and characterization of microcapsules containing linseed oil and its use in self-healing coatings, Prog. Org.

Coat. 63 (2008) 72-78.

[17] M. Behzadnasab, M. Esfandeh, S.M. Mirabedinia, M.J. Zohuriaan-Mehra, R.R. Farnoodb, Preparation and characterization of linseed oil-filled urea-formaldehyde microcapsules and their effect on mechanical properties of an epoxy-based coating, Colloid. Surface. A. 457 (2014) 16-26.

[18] K. Thanawala, N. Mutneja, A.S. Khanna, R.K. Singh Raman, Development of self-healing coatings based on linseed oil as autonomous repairing agent for corrosion resistance, Materials 7 (2014) 7324-7338.

[19] T. Szabó, J. Telegdi, L. Nyikos, Linseed oil-filled microcapsules containing drier and corrosioninhibitor -Their effects on self-healing capability of paints, Prog. Org. Coat. 84 (2015) 136-142.

[20] H. Es-haghi, S.M. Mirabedini, M. Imani, R.R. Farnood, Preparation and characterization of pre-silane modified ethylcellulose-based microcapsules containing linseed oil, Colloid. Surface. A. 447 (2014) 71-80.

[21] M. Samadzadeh, S. Hatami Boura, M. Peikari, A. Ashrafi, M. Kasiriha, Tung oil: An autonomous repairing agent for self-healing epoxy coatings, Prog. Org. Coat. 70 (2011) 383-387.

[22] N.W. Khun, H. Zhang, X.Z. Tang, C.Y. Yue, J.L. Yang, Short carbon fiber-reinforced epoxy tribomaterials self-lubricated by wax containing microcapsules, J. Appl. Mech. 81 (2014) 121004.

[23] N.W. Khun, H. Zhang, C.Y. Yue, J.L. Yang, Self-lubricating and wear resistant epoxy composites incorporated with microencapsulated wax, J. Appl. Mech. 81 (2014)

071004.

[24] N.W. Khun, H. Zhang, D.W. Sun, J.L. Yang, Tribological behaviors of binary and ternary epoxy composites functionalized with different microcapsules and reinforced by short carbon fibers, Wear 350 (2016) 89-98.

[25] N.W. Khun, W.H. Zhang, J.L. Yang, E. Liu, Tribological performance of silicone composite coatings filled with wax-containing microcapsules, Wear 296 (2012) 575-582.

[26] H.Y. Li, Q. Wang, M.L. Li, Y.X. Cui, Y.J. Zhu, B.H. Wang, H.Y. Wang, Preparation of high thermal stability polysulfone microcapsules containing lubricant oil and its tribological properties of epoxy composites, J. Microencapsul. 33 (2016) 286-291.

[27] Q.B. Guo, K.T. Lau, B.F. Zheng, M.Z. Rong, M.Q. Zhang, Imparting ultra-low friction and wear rate to epoxy by the incorporation of microencapsulated lubricant, Macromol. Mater. Eng. 294 (2009) 20-24.

[28] Q.B. Guo, K.T. Lau, M.Z. Rong, M.Q. Zhang, Optimization of tribological and mechanical properties of epoxy through hybrid filling, Wear 269 (2010) 13-20.

[29] G.W. Ma, X.F. Xu, Q.B. Jin, R.J. He, J.J. Guan, Preparation and tribological behavior of RC 2540-melamine-formaldehyde resin microcapsulesm, Acta. materiae. Compositae. Sinica. 30 (2013) 37-43.

[30] N.W. Khun, D.W. Sun, M.X. Huang, J.L. Yang, C.Y. Yue, Wear resistant epoxy composites with diisocyanate-based self-healing functionality, Wear 313 (2014) 19–28.

[31] P. Bandeira, J. Monteiro, A.M. Baptista, F.D. Magalhaes, Tribological performance of PTFE-based coating modified with microencapsulated [HMIM][NTf_2] ionic liquid, Tribol. Lett. 59 (2015) 1-15.

[32] S. Armada, R. Schmid, S. Equey, I. Fagoaga, N. Espallargas, Liquid-solid self-lubricated coatings, J. Therm. Spray. Technol. 22 (2013) 10-17.

[33] M.M. Yang, X.T. Zhu, G.N. Ren, X.H. Men, F. Guo, P.L. Li, Z.Z. Zhang, Tribological behaviors of polyurethane composite Coatings filled with ionic liquid core/silica gel shell microcapsules, Tribol. Lett. 58 (2015) 1-9.

[34] B. Pena, T. Gumi, State of the art of polysulfone microcapsules. Curr. Org. Chem. 17 (2013) 22-29.

[35] C. Panisello, B. Pena, T. Gumi, R. Garcia-Valls. Polysulfone Microcapsules with Different Wall Morphology. J. Appl. Polym. Sci. 129 (2013) 1625-1635.

[36] L. Yan, H.Y. Wang, C. Wang, L.Y. Sun, D. Liu, Y.J. Zhu, Friction and wear properties of aligned carbon nanotubes reinforced epoxy composites under water lubricated condition, Wear 308 (2013) 105-112.

[37] H.Y. Li, Q. Wang, H.Y. Wang, Y.X. Cui, Y.J. Zhu, B.H. Wang, Fabrication of thermally stable polysulfone microcapsules containing [EMIm][NTf_2] ionic liquid for enhancement of in-situ self-lubrication effect of epoxy, Macromol. Mater. Eng. 301 (2016) 1473-1481.

[

Figure Captions:

Figure 1 The schematic of microencapsulation mechanism

Figure 2 Schematic diagram of the friction and wear tests

Figure 3 SEM micrographs and size distribution of tung oil-loaded microcapsules (a) microcapsules magnification：100× (b) microcapsules magnification：200× (c) ruptured microcapsule (d) size distribution

Figure 4 FTIR spectra of microcapsules, PSF and tung oil

Figure 5 TGA curves of PSF, tung oil filled microcapsules and tung oil

Figure 6 Optical photographs of corrosion protection of steel plates: (a1-a4) pure control epoxy scratched coating with immersion time of 0, 1, 4, 7 days, (b1-b4) self-healing epoxy scratched coating by incorporating 10 wt% microcapsules with immersion time of 0, 1, 4, 7 days

Figure 7 SEM micrographs of the scratched area of (a) control coating, (b) self-healing coating with 10 wt% microcapsules

Figure 8 Schematic diagram of self-healing mechanism

Figure 9 Frictional coefficients and specific wear rate of self-lubricant coating versus content of the Tung oil-loaded microcapsules

Figure 10 The schematic diagrams of antifriction mechanism of self-lubricating coating

Figure 11 SEM images of the worn surface (a) control coating (b) self-lubricating coating filled with 10 wt% tung oil-loaded microcapsules (c) close view of a cavity left by the ruptured microcapsule. The arrows indicate the sliding direction.

Graphical abstract：