Effect of PDMS Viscosity and Additive Amount of Curing Agent Solution on the Mechanical Properties of PDMS Fouling Release Coating

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Abstract. The mechanical properties of PDMS fouling release coatings have a very important effect on actual use. The coating was designed and prepared to study the effect of viscosity of PDMS resin and additive amount of curing agent on the mechanical properties of the coating. The cross-linking index of the coating was used to analyze the mechanical properties of the coatings. The results indicate that the mechanical properties of the coating formed by the crosslinking reaction with a high viscosity of PDMS resin are better. Despite the different viscosity of PDMS resin, the coating has the best mechanical properties, when the mole ratio of PDMS to TEOS is 1: 18.24.

1. Introduction
For maritime and aquatic industries, the marine fouling organism can accumulate on man-made surfaces, which would lead to the increase of ship’s dead-weight, hull roughness, and hydrodynamic drag. Subsequently, the fouling process can damage and corrodes the structure of equipment immersed in seawater bodies while it also increased the cost of the economy[1, 2]. It is a worldwide problem for the shipping industry, and one of the most effective, economical, and convenient method is to brush antifouling coating. In recent years, ecological safety, environmental protection problems have attracted more attention[3]. Herein, an environmentally friendly antifouling coating which will not release toxic to the seawater has been used, especially on fouling-release coatings. Fouling release coatings provide a surface that can reduce the adhesion strength of fouling organisms enabling cleaning by pressurized water jets or seawater erosion[4, 5]. Fouling release coatings based on polydimethylsiloxane (PDMS) become the focus of the development of new antifouling coatings.

A great deal of investigation has been conducted on this coating, which appears to be a viable fouling-release coating system. The main factors affecting the antifouling properties of the coating are surface free energy, elastic modulus, thickness, polarity, and surface smoothness[6, 7]. Specifically, it is experimentally confirmed that adhesion ability is proportional to the square root of the value which equals the value of elastic modulus multiplied by the value of surface free energy[4, 8, 9].

Although the antifouling performance of fouling release coating based on PDMS can be improved by decreasing the elastic modulus of coating, the low mechanical properties will greatly weaken the practical use of the coating. In general, the studies on enhancement of the mechanical properties of the PDMS coating are focused on two aspects: chemical modification or powder enhancement. In this paper, based on PDMS, fouling release coatings were prepared to consist of different viscosity of PDMS resin,
and changing the additive amount of curing agent. The mechanical properties of the coatings were investigated by cross-linking index.

2. Experimental materials and methods

2.1 Experimental materials

To observe the properties of PDMS fouling release coating with different additive amounts of curing agent solution, the composition of the coating was designed as a three-component system in Table 1. PDMS was obtained from Dayi Chemical Industry Co., Ltd., with formula HO-Si(CH3)2O(Si(CH3)2O)nSi(CH3)2-OH and viscosity of 2800 mm²/s, 5000 mm²/s, and 10000 mm²/s. The curing agent solution (Part B) is composed of tetraethylorthosilicate (TEOS) and xylene, with a volume ratio of 3:7. The catalyst solution (Part C) consists of dibutyltin dilaurate (DBTDL) and acetylacetone, and the volume ratio of these two compounds is also 3:7. The above four compounds are derived from Tianjin Kemiou Chemical Reagent Co., Ltd.

2.2 Preparation of coatings

Glass slides with dimensions of 75 mm × 25 mm × 1 mm and Teflon mold with dimensions of 150 mm × 150 mm × 3 mm were used for this investigation. The faces of panels were painted by studied coatings and cured in ambient for at least 7 days. The paint number is short for Pxx-By, in which x represents the viscosity of PDMS in coating and y represents the mass of curing agent solution.

| Component | PDMS (mm²/s) | Curing agent solution | Catalyst solution |
|-----------|--------------|-----------------------|-------------------|
|           | 2800         | 5000                  | 10000             | 2/3/4/5/6/7       |
| Content (g)| 20           | 2/3/4/5/6/7           | 1                 |

2.3 Experimental methods

The cross-linking index of coating samples was determined by equilibrium swelling method, and the use of solvent is toluene (analytical grade) which was bought from Yongda Chemical Reagent Co., Ltd. Formula (1) can calculate the values of the relative molecular mass between crosslinking points (M_c), and it is usually to represent the cross-linking index. The greater M_c of coating is, the lower the cross-linking index of coating is. In this formula, v represents the reciprocal of equilibrium swelling ratios of samples, \( \rho \) represents the density of samples before swelling, \( V \) represents the molar volume of solvent and it is 106.125 cm³/mol for toluene, \( \chi_1 \) refers to the Flory-Huggins interaction parameter of samples and toluene and it is 0.45 in this experiment. The whole experiment was carried out at 25 °C.

\[
M_c = \frac{-\rho V \left( v^2 - v/2 \right)}{\ln(1 - v) + v + \chi_1 * v^2}
\]

Tensile samples were prepared into strips with 150 mm × 20 mm × 2 mm and then stretched on a Labthink XLM auto tensile tester. Elastic modulus was fitted with the data in which the strain is less than 0.2 mm/mm. The hardness of samples was tested by the HT220 shore hardness tester, and the prepared membrane needed to be folded repeatedly to exceeding 5 mm, which was required by the equipment.

3. Results

3.1 The cross-linking index of samples

The results showed that the M_c of coating samples changed with the changes of curing agent solution, as showed in Fig. 1. It also reflects that the M_c of coatings reacted by different viscosity of PDMS resin is also different. With the increase of the additive amount of curing agent solution, the value of M_c of coating samples increases firstly and then decreases. Under the condition of the same additive amount
of curing agent solution, the higher the viscosity of PDMS resin is, the smaller value of $M_c$ displays, which means the higher cross-linking index of samples.

$$\text{Fig. 1. The } M_c \text{ of studied coating samples}$$

3.2 Mechanical properties of samples

The tensile properties of coating samples in which the viscosity of PDMS resin is 10000 mm$^2$/s were examined, and the results were shown in Fig. 2. Fig. 2(a) shows the tensile curves of the samples, it indicated that 100% tensile stress increased accordingly with the increasing additive amount of curing agent solution. Fig. 2(b) revealed that the elastic modulus and shore hardness changed with changes of the additive amount of curing agent. It means that the elastic modulus and shore hardness is related to the cross-linking index. Specifically, the elastic modulus and shore hardness increased rapidly with the increasing cross-linking index of the sample.

$$\text{Fig. 2. Tensile properties of coating sample with the 10000 mm}^2/\text{s viscosity of PDMS resin: (a) stress-strain curves and (b) dependency of elastic modulus and shore hardness on the additive amount of curing agent.}$$

4. Discussion

For the three-dimensional structure of PDMS fouling release coating, the cross-linking index reflects the intensity of the structure. Coatings with a high cross-linking index have better mechanical properties. In this experiment, when the value of the cross-linking index of coating reacted by different viscosity of PDMS resin was up to the maximum, the additive amount of curing agent was different. And the higher the viscosity of PDMS resin is, the less the additive amount of curing agent is under the maximum value of a cross-linking index. Formula (2) can calculate the relative molecular mass of PDMS resin, where $\eta$
represents the viscosity of PDMS resin and \( M_n \) represents the relative molecular mass of PDMS resin. And Table 2 lists the mole ratio of PDMS resin to TEOS when the cross-linking index value of coating is the maximum. From Table 2, it could be confirmed that the mole ratio of coating with different viscosity of PDMS resin is the same at the maximum cross-linking index. The optimum mole ratio of PDMS resin to TEOS is 1:18.24. The lower the viscosity of PDMS resin is, the smaller the relative molecular mass of PDMS resin is, and the more the amount of substance of PDMS resin is under the same mass, so the mass of the curing agent is also more.

\[
\log \eta = 1.00 + 0.0123 M_n^{0.5}
\]  

(2)

Table 2. The mole ratio of PDMS resin to TEOS with the maximum cross-linking index of coating.

| Viscosity   | Relative molecular weight | Mass ratio of PDMS resin to curing agent | Mole ratio of PDMS resin to TEOS |
|------------|--------------------------|----------------------------------------|---------------------------------|
| 2800 (mm²/s) | 39867                    | 20:6                                   | 1:18.24                         |
| 5000 (mm²/s) | 48462                    | 20:5                                   | 1:18.24                         |
| 10000 (mm²/s)| 59836                    | 20:4                                   | 1:18.24                         |

When the mole ratio of PDMS to TEOS is 1:18.24, the value of the cross-linking index of coating is the maximum. So the effect of viscosity of PDMS resin on the mechanical properties of the coating was observed in Fig. 3 under that proportional condition. The mechanical properties results are shown that the higher the viscosity of PDMS resin is, the less the value of \( M_c \) of coating displays, the greater the cross-linking index of coating is, the better the mechanical properties of the coating are. This is due to the high viscosity of PDMS resin has a large relative molecular mass, so the three-dimensional structure is more complex and dense.

![Fig. 3. Tensile properties of coating sample which the mole ratio of PDMS to TEOS is 1:18.24: (a) stress-strain curves and (b) dependency of elastic modulus and shore hardness on the viscosity of PDMS resin.](image)

5. Conclusion

For studied coating, the observation results also indicate that the mechanical properties of the coating are affected by the additive amount of curing agent and the viscosity of PDMS resin. The coating reacted by the high viscosity of PDMS resin has a high cross-linking index and has good mechanical properties. When the mole ratio of PDMS resin and TEOS is 1:18.24, the coating has the highest cross-linking index and the best mechanical properties. For different viscosity of PDMS resin, the mole ratio of PDMS to TEOS is unchanged when the mechanical properties of the coating are the best.

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References

[1] S. Pinteus, M.F.L. Lemos, C. Alves, J. Silva, R. Pedrosa, The marine invasive seaweeds Asparagopsis armata and Sargassum muticum as targets for greener antifouling solutions, Science of the Total Environment, 750 (2021).
[2] F.-x. Fan, Y.-m. Zheng, M. Ba, Y.-f. Wang, J.-j. Kong, J.-h. Liu, Q. Wu, Long time super-hydrophobic fouling release coating with the incorporation of lubricant, Progress in Organic Coatings, 152 (2021).

[3] P. Hu, Q.Y. Xie, C.F. Ma, G.Z. Zhang, Silicone-Based Fouling-Release Coatings for Marine Antifouling, Langmuir, 36 (2020) 2170-2183.

[4] F. Azemar, F. Fay, K. Rehel, I. Linossier, Ecofriendly silicon-poly(lactic acid) hybrid antifouling coatings, Progress in Organic Coatings, 148 (2020).

[5] M. Ba, Z.P. Zhang, Y.H. Qi, The influence of MWCNTs-OH on the properties of the fouling release coatings based on polydimethylsiloxane with the incorporation of phenylmethylsilicone oil, Progress in Organic Coatings, 130 (2019) 132-143.

[6] W.J. Yang, K.-G. Neoh, E.-T. Kang, S.L.-M. Teo, D. Rittschof, Polymer brush coatings for combating marine biofouling, Progress in Polymer Science, 39 (2014) 1017-1042.

[7] T.P. Galhenage, D. Hoffman, S.D. Silbert, S.J. Staślien, J. Daniels, T. Miljkovic, J.A. Finlay, S.C. Franco, A.S. Clare, B.T. Nedved, M.G. Hadfield, D.E. Wendt, G. Waltz, L. Brewer, S.L.M. Teo, C.S. Lim, D.C. Webster, Fouling-Release Performance of Silicone Oil-Modified Siloxane-Polyurethane Coatings, ACS Appl Mater Interfaces, 8 (2016) 29025-29036.

[8] S.B. Ulaeto, R. Rajan, J.K. Pancrecious, T.P.D. Rajan, B.C. Pai, Developments in smart anticorrosive coatings with multifunctional characteristics, Progress in Organic Coatings, 111 (2017) 294-314.

[9] M. Ba, Z. Zhang, Y. Qi, Fouling Release Coatings Based on Polydimethylsiloxane with the Incorporation of Phenylmethylsilicone Oil, Coatings, 8 (2018).