Synthesis and characterization of a novel hydroxy terminated polydimethylsiloxane and its application in the waterborne polysiloxane–urethane dispersion for potential marine coatings

Hamid Javaherian Naghash*, Iman Mohammadidehcheshmeh and Mohammadmilad Mehrnia

α-Butyl α-N, N-dihydroxyethyl aminopropylpolymethylhydrosiloxane (PDMS), a monotelechelic polydimethylsiloxane with a diol-end group, which is used to prepare siloxane–urethane dispersion, was successfully synthesized. Then, novel silicone-based polyurethane (PU)-dispersion was prepared by the addition polymerization of hexamethylene diisocyanate, to PDMS, polyethylene glycol (PEG) and dimethylol propionic acid. The goal of this study was to explore the potential use of polysiloxane–urethane in marine coatings in order to boost the flexibility, adhesion, erosion and foul-release property with respect to PDMS/PEG ratio (PDMS wt%). The PDMS was characterized by Fourier-transform infrared (FT-IR), proton nuclear magnetic resonance and carbon-13 nuclear magnetic resonance spectroscopic techniques. The results showed that each step was successfully carried out and the targeted products were synthesized in all cases. The structural elucidation of the synthesized waterborne PU and waterborne polysiloxane–urethane (WBPSU) was carried out by FT-IR spectroscopic technique. Thermal properties of the resins were studied by using thermogravimetric analysis and differential scanning calorimetry. The antifouling property of the coatings was investigated by the immersion test under a marine environment for 90 days. The fouled area was calculated for all the samples, and the fouled area (%) decreased with increasing PDMS content. After 90 days, the lowest fouled area (6%) was observed in the sample using WBPSU2 (PDMS 4.48 wt%) among all of the samples. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: coating; siloxane; marine environment; polyurethane

INTRODUCTION

It is well known that polysiloxanes possess a variety of unique and superior properties, such as low surface energy, good water resistance and so on.\textsuperscript{[1,2]} Hence, polysiloxanes exhibit dual virtues of organic and inorganic materials. Copolymerization of polysiloxanes with reactive functional groups and other organic polymers can endow the organic polymers with the excellent properties of polysiloxanes so that new polymer materials with special properties can be obtained.\textsuperscript{[3,4]} It is an effective way to advance mechanics performance of polysiloxanes and to introduce its virtues into other polymers. Difunctional polysiloxanes are often used for the synthesis of polyurethane (PU)–polysiloxane graft or block polymers. The difunctional hydroxyalkyl terminated polysiloxanes are especially useful to produce waterborne PUs modified with polysiloxanes, particularly for preparation of aqueous PU dispersion. On the other hand, marine biological fouling, usually termed marine biofouling, can be defined as the undesirable accumulation of microorganisms, plants and animals on artificial surfaces that are exposed to the marine environment. This phenomenon is clearly observed on every suitable substrate such as ship hulls, marine cages, pipelines, heat exchangers and other structures including offshore platforms and bridges which are immersed in seawater.\textsuperscript{[5]} In this case, one of the most promising technologies is a non-stick foul-release coating,\textsuperscript{[6]} which can prevent the adhesion of organisms by providing a low-friction, ultra-smooth surface that makes the attachment of a fouler very difficult and the detachment easy. Potential candidates for this coating include fluoropolymer and siloxane-based coatings.\textsuperscript{[5,7,8]} Ideally these “non-stick” coatings would completely prevent the attachment of foulers. However, fouling can occur on real ship panels employing non-stick coatings,\textsuperscript{[9,10]} even though these coatings significantly limit the strength of the joint between the fouler and hull, making the bond so weak that it can be broken by the weight of the fouler or the motion of the ship through the water. Therefore, more realistically, toxic antifouling paints can be replaced by non-stick coatings

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combined with the periodic removal of the fouling organisms under water using brushes, which is an alternative to cleaning in dry-docks.\textsuperscript{6,9} This combined technique could be an attractive alternative to the use of anti-foucing materials.\textsuperscript{6,10,11} Today, non-biocidal, silicone-based foul-release coatings are commercially available and minimize the adhesion of the attached organisms.\textsuperscript{6,10,11} These attached organisms can be removed easily when the vessel moves through the water. However, these coatings are expensive and less robust than biocidal paints, and their application is limited to fast vessels (15–30 knots) with a quick turn-around.\textsuperscript{10–12} Research has now focused on the development of new anti-adhesive coatings that combine low adhesion properties on the “water side” to resist the attachment of the organisms in aquatic environments and high adhesion on the “substrate side” to facilitate the firm bonding to the protected object, combined with a high degree of mechanical strength.\textsuperscript{10–12} Current commercial marine paints contain a large amount of volatile organic solvents,\textsuperscript{13,14} which are released into the atmosphere during the drying stage. These harmful solvents also threaten the human body.\textsuperscript{13,14} Many countries have already restricted the emission of these harmful solvents.\textsuperscript{14} Therefore, the marine coating must be made environmentally friendly as well as free from all kinds of pollution. Although many polymers are promising as a foul-release coating, their syntheses and applications require a large amount of organic solvent. Ideally, the polymer should be processable under moderate conditions with no (or less) volatile evolution and should be stable in a marine environment.\textsuperscript{6} Further, the polymer must be compatible with the additive and pigment and exhibit good foul-release properties. Only a few polymer coatings are commercially available because of an unfavorable combination of price, processability and performance. These polymers are often made and used for specialized applications.\textsuperscript{15–18} It has been shown that polydimethylsiloxane (PDMS) can be useful for foul-release type coatings due to its non-stick surface.\textsuperscript{16} Unfortunately, a key disadvantage of using PDMS is its poor adhesion and bulk mechanical properties.\textsuperscript{16,17} Thus, over the last few years, a significant effort has been underway to overcome these limitations using other polymers such as epoxide and PU with PDMS.\textsuperscript{16–18} However, it is hard to find the exact chemical composition of PDMS with PU. As PDMS has low free energy\textsuperscript{16} and PU has good elastomeric properties,\textsuperscript{13} the exact combination of PDMS in PU can be effective for antifouling properties while boosting suitable mechanical properties. In this report, waterborne polysiloxane–urethanes (WBPUS) were synthesized, and the WBPUS coatings contain mainly water and do not emit organic solvent at any stage of synthesis or during application at drying stage. Thus, the synthesized waterborne coatings meet the environmental legislations.\textsuperscript{5–7,14,15,19}

In this study, WBPUS were synthesized using hydroxy terminated PDMS (Mn = 2410) with polyethylene glycol (PEG) (Mn = 10000) as a soft segment. The structure of these PU s was characterized by Fourier-transform infrared (FT-IR) spectroscopic technique. The molecular weight and mechanical properties (tensile strength and Young’s modulus) of the films were characterized with respect to PDMS content. The polymer surface was characterized by AFM technique. The synthesized waterborne resin was coated onto PVC and immersed in sea water for 90 days. We checked the antifouling performance of immersed coatings after a certain interval. Photographs of the coatings were taken, and the fouled area was calculated to justify the antifouling performance for all samples.

## EXPERIMENTAL

### Materials and equipment

Hexamethyldisilazane, 3-chloropropene, hexachloroplatinic acid hydrate, toluene, methanol, acetic acid, poly (methyl hydrogen siloxane), diethanolamine, dibutyltin dilaurate (DBT), PEG 10000 and tetrahydrofuran, were supplied by Merck, Hohenbrunn, Germany, and were used as received. Acetone was purchased from Fluka and immersed in 4Å molecular sieves (Zeolite A) for a week. Hexamethylene disiocyanate (HMDI), dimethyl propionic acid (DMPA) and triethylamine (TEA, Junsei) were used without further purification. Double-distilled and de-ionized water was used throughout. FT-IR spectroscopy analysis was performed with a Nicolet Impact 400D Model spectrophotometer (Nicolet Impact, Madison, USA) using KBr pellets. The spectra were obtained over the wave number range 4000–400 cm\textsuperscript{-1} at a resolution of 2 cm\textsuperscript{-1} using an MCT detector with co-addition of 64 scans. NMR Spectra were recorded on a Bruker AV600 NMR Spectrometer (\textsuperscript{1}H, 600 MHz, \textsuperscript{13}C, 150 MHz). Chemical shifts were reported in ppm and referenced to residual solvent resonances (\textsuperscript{1}H, \textsuperscript{13}C) or an internal standard. The mean particle size of the dispersions was measured using laser-scattering equipment (Autosizer, Malvern IIC, Malvern, Worcester, UK) at 25 °C. Diffractive scanning calorimetry (DSC) thermograms were taken on a Mettler TA 4000 Model apparatus at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) measurements of copolymers were carried out by a DuPont TGA 951 under nitrogen atmosphere at a heating rate of 10°C/min. A gel permeation chromatograph (Model 500, Analytical Scientific Instruments, USA) with a refractive index detector (RI2000, Schambeck, Germany) was used in contact mode.

**Synthesis of bis (2-(trimethylsilyloxy) ethyl) amine (TSEA)**

About 90.50 g (0.56 mol) of hexamethyldisilazane was slowly added to 52.25 g (0.5 mol) of diethylolamine. The reaction was carried out in a 500-ml round-bottomed three-necked flask equipped with a magnetic stir bar, condenser and thermometer.\textsuperscript{20} The reaction mixture was stirred at reflux for 8 h, then the final mixture was vacuum distilled under 5 mmHg, and the distillate from 104 to 106 °C was collected with a yield of 93%. The preparation procedure is illustrated in Scheme 1. FT-IR (KBr, cm\textsuperscript{-1}): 3338 (N–H), 1525, 841 (Si–CH\textsubscript{3}), 1099 (Si–O–C). Proton nuclear magnetic resonance (\textsuperscript{1}H-NMR) (CDCl\textsubscript{3}, 600 MHz, δ ppm): 0.03–0.22 (m, 18 H, Si–CH\textsubscript{3}), 1.85 (s, 1 H, NH), 2.73–2.75 (t, 4 H, CH\textsubscript{2}), 3.31–3.37 (m, 4 H, CH\textsubscript{2}), 4.12–4.17 (d, 2 H, Si–CH\textsubscript{3}).

**Scheme 1.** Synthesis of bis (2-(trimethylsilyloxy) ethyl) amine (TSEA).

Synthesis of N, N-bis(2-(trimethylsilyloxy)ethyl)allylamine (TSAA)

About 24.90 g (0.10 mol) of TSEA was prelocated into a round-bottomed flask, and then 3.83 g (0.05 mol) of 3-chloropropene was added into the flask under agitation. The reaction solution was stirred at 55 °C for one h, followed by filtration to remove the ammonium. The alkylation product was separated through distillation under reduced pressure (5 mmHg) from the filtrate above, and the distillate between 118 and 120 °C was collected as a colorless liquid. The preparation procedure is illustrated in Scheme 2. FT-IR (KBr, cm⁻¹): 3078 (~C–H), 1642 (C = C), 1251, 841 (Si–CH₃), 1100 (Si–O–C). ¹H-NMR (CDCl₃, 600 MHz, δ ppm): 0.07–0.22 (m, 18H, Si–CH₃), 2.65–2.69 (t, 4H, N–CH₂), 5.19–3.22 (t, 2H, N–CH₂–CH₂ = CH₂), 3.63–3.65 (t, 4H, O–CH₂), 5.12–5.19 (m, 2H, =CH₂), 5.82–5.89 (m, 1H, =CH₂). 13C-NMR (CDCl₃, 150 MHz, δ, ppm): 1.46 (C–Si), 51.37 (C–N), 61.72 (C–O), 61.66 CH₂–(CH₂)₂–N, 117.56 CH₂ = CH, 135.82 CH₂ = (CH–CH₂). Purity: 97%. Elemental analysis calculated for C₁₃H₃₃Si₂O₂N (%): C 53.98, H 10.73, N 4.84, O 11.07. Found: C 53.88, H 10.72, N 4.87, O 11.13.

Synthesis of ω-N, N-bis(trimethylsilyloxyethyl)aminopropyl-polymethylhydrosiloxane (TSAP)

A 100-ml round-bottomed flask, equipped with a stirrer, a thermometer, a nitrogen purge and a reflux condenser (the later equipped with a tubular dryer filled with anhydrous calcium chloride), was charged with excessive TSAA, 25 ml of toluene and 40 μl of chloroplatinic acid solution (2% in isopropanol). The flask was heated to 90 °C, followed by drop-wise addition of 19.03 g (84.0 mmol) of PMHS and kept at this temperature for 8 h. Toluene and excessive TSAA were removed under vacuum. The hydrosilylation product was obtained with a yield of 82%. The preparation procedure is illustrated in Scheme 3. FT-IR (KBr, cm⁻¹): 1269 and 847 (Si–CH₃), 1055 (Si–O–C), 2164 (Si–H), 3411 (~O–H). ¹H-NMR (CDCl₃, 600 MHz, δ ppm): 0.02–0.32 (m, 141H, Si–CH₃), 1.25–1.3 (t, 2H, Si–CH₃), 1.75–1.80 (m, 2H, CH₂–(CH₂)₂–CH₂), 2.35–2.45 (T, 2H, N–(CH₂)₂CH₂), 2.75–2.80 (T, 4H, N–CH₂–CH₂), 3.72–3.80 (t, 4H, O–CH₂), 4.75–4.80 (S, 34H, Si–H). 13C-NMR (CDCl₃, 150 MHz, δ, ppm): 0.91 (C–Si–CH₃), 1.21, 1.63 and 2.93 (C–Si–O–Si), 17.47 (Si–CH₂), 27.48 CH₂–(CH₂)–CH₂, 59.52 CH₂–(CH₂)–N, 61.81 N–(CH₂)–CH₂–O, 62.81 (CH₂–O).

Synthesis of WBPU and WBPSU dispersions

A 500-ml, round-bottomed, four-necked-flask, separable glass reactor with mechanical stirrer, thermometer, condenser and nitrogen purge was used. Polyaddition reaction was carried out under a N₂ atmosphere in a constant-temperature water bath. HMDI, PEG and PDMS were first charged into the reactor and heated to 80 °C under moderate stirring (200 rpm). Then, DBT was dropped into the reactor while keeping the temperature at 80 °C. The reaction proceeded over approximately 1 h, DMPA

Scheme 2. Synthesis of N, N-bis(2-(trimethylsilyloxy)ethyl)allylamine (TSAA).


Scheme 4. Synthesis of ω-N, N-bis(dihydroxyethylaminopropyl) polymethylhydrosiloxane (PDMS).
was subsequently charged and reaction proceeded for another 2 h at the same temperature, upon which the theoretical NCO/OH value of 1.2. was determined by the dibutylamine back titration. Then, methyl ethyl ketone (0 wt%) was added to the NCO-terminated prepolymer mixture at 65°C in order to adjust the viscosity of the solution. This WBPSU dispersions was then neutralized by the addition of TEA at 25°C, followed by dispersion at high speed (1500 rpm) with distilled water which was added drop-wise to produce a WBPSU dispersion (Schemes 5 and 6).

Preparation of WBPU and WBPSU films

The films were prepared by pouring the aqueous dispersion (5 g) onto a Teflon disk (diameter 5 cm) and drying the dispersion under ambient conditions for about 48 h. The films (typically about 0.5-mm thick) were dried at 60°C for 6 h and then vacuum dried for another 12 h. The vacuum dried films were stored in a desiccator at room temperature.

Supports mounting coatings onto PVC solid supports

For the field tests, the synthesized waterborne resins were mounted onto flat PVC solid supports through the air-spraying method. The coated samples were fully dried within 4 h at ambient temperature, and the dried samples were used in the immersion tests. Normal antifouling coatings are applied on the steel structures, but in this report, we used the PVC substrate because we investigated the antifouling property of coating systems excluding the corrosion phenomena by the sea water.

Field tests in seawater

The antifouling field tests were performed according to the ASTM D3623 specifications from August 2011 until November 2011 (90 days) located at Persian Beach in Kish Island, Islamic Republic of Iran. The samples that were mounted onto the PVC supports were immersed into the seawater at depths of about 1 m below the surface. The samples faced the open ocean and were not caged. Periodically, the samples were removed and photographed. We calculated the fouled area (%) using the image analysis software AxioVision Release 4.5 (Carl Zeiss).

Water absorption

Dried films (30 mm × 30 mm; original weight designated as \(W_0\)) were immersed in water for 24 h at 25°C. After the residual water was wiped from the films using filter paper, the weight (\(W_1\)) was measured immediately. It was calculated as follows:

\[
\text{water absorption, } R(\%) = \left( \frac{W_1 - W_0}{W_0} \right) \times 100
\]

RESULTS AND DISCUSSIONS

Synthesis and characterization of TSEA and TSAA

Bis(2-trimethylsilyloxy)ethyl)amine and \(N,N\)-bis(2-(trimethylsilyloxy)ethyl) allylamine were prepared via hydroxyl protection and alkylation reaction as depicted by Schemes 1 and 2. Diethyloleamine was first protected by hexamethyldisilazane via hydroxyl protection, particularly because dehydrogenation reaction can occur between hydroxyl group and Si–H group of H-containing silicone oil. On the other hand, if alkylation reaction between diethylamine and 3-chloropropene was first carried out, there exist a lot of difficulties in filtering to remove the ammonium salt. In contrast, when hydroxyl protection occurred before alkylation reaction, the boiling point and viscosity of hydroxyl protection product were reduced so that the product was easy to be separated and purified. When utilizing GC to follow the reaction process, GC showed that there was an unknown peak whose retention time was at 8.5 min. In comparison with the retention time of reactants, we supposed that the peak at 8.5 min was the peak of hydroxyl protection product. To validate our guess, the product was separated under vacuum and subjected to characterization. Its refractive index was measured as being \(n_D^{25} = 1.4196\). The product was subjected to FT-IR analysis. FT-IR spectrum of the product which was presented in Fig. 1(a) showed that there was a weak amino vibration peak at 3338 cm\(^{-1}\). In addition, Si–CH\(_3\) vibration and Si–O–C...
vibration peaks were also observed in the spectrum of the TSEA. Then, the same compound was subjected to 1H-NMR and carbon-13 nuclear magnetic resonance (13C-NMR) analysis. 1H-NMR spectrum (Fig. 2) revealed that there were four peaks which are easily recognized from the chemical shifts and the peak area integrations. Figure 3 indicated the 13C-NMR spectra of TSEA. The number of carbons in the TSEA was compatible with the number of spectra. In the second step, the GC spectrum of the filtrate displayed another manifest peak with retention time at 10 min. The product, assumingly the alkylation TSAA, was also separated under vacuum, and its refractive index was $n^\mathrm{D}_{25} = 1.4292$. The product was first subjected to FT-IR analysis Fig. 1(b). Comparing with the spectrum of TSEA, the spectrum of TSAA exhibited the following main characteristics: A weak amino vibration peak disappeared completely at $3338 \text{ cm}^{-1}$ and $C = C$ double bond vibration appeared at $1642 \text{ cm}^{-1}$. And other peaks, Si–CH$_3$ vibration and Si–O–C vibration, were also present in the spectrum of the TSAA. In the Fig. 4 the spectrum of 1H-NMR revealed that the chemical shifts of the peaks at 2.74 and 3.70 ppm of TSAA were kept.
in the same order comparing with the spectrum of the TSEA, particularly because their chemical circumstances were not changed. Also, Fig. 5 indicated the $^{13}$C-NMR spectra of TSAA. The number of carbons in the TSAA was compatible with the number of spectra. From the chemical shifts and the peak area integrations of six peaks, the peaks representing protons on the chain of TSAA were easily recognized. The spectra of FT-IR, $^1$H-NMR and $^{13}$C-NMR of TSEA and TSAA showed that the hydroxyl protection product and alkylation product possessed the structures as we desired and their elemental compositions were $C_{10}H_{27}O_{2}Si_2Na$ and $C_{13}H_{31}O_{2}Si_2N$.

**Synthesis and characterization of TSAP and PDMS**

The TSAP and PDMS were synthesized through hydrosilylation, and deprotection as outlined in Schemes 3 and 4. Since the Si–H group can undergo the hydrosilylation reaction to add to unsaturated allyl compounds. The reaction products were subjected to FT-IR, $^1$H-NMR and $^{13}$C-NMR analyses (Figs. 1 (C and D), 6–9). The main characteristic of FT-IR spectrum of H-containing silicone oil was that a strong Si–H vibration appeared at 2166 cm$^{-1}$. $^1$H-NMR spectrum also revealed that the peak at 4.63 ppm was assigned to Si–H. Comparing with the spectra of compound TSAA and TSAP, the hydrosilylation product mainly represented the following characteristics: Complete disappearance of C=C double bond vibration at 1642 cm$^{-1}$. This indicated that hydrosilylation reaction had happened between C=C double bond and Si–H. Meanwhile the data of $^1$H-NMR spectrum of hydrosilylation product TSAP including chemical shifts and peak area integrations also validated the occurrence of hydrosilylation reaction. To create hydroxyl groups in the molecule, the hydrosilylation product TSAP was deprotected so that it became reactive towards isocyanate group in a subsequent step to
prepare siloxane modified PU. Because the Si–O–C bond was not stable in the presence of base or acid and easy to rupture, excessive methanol was added into the hydrosilylation product TSAP in the presence of acetic acid as catalyst to produce hydroxyl groups. In this step, it is possible that the tertiary amine would change into an ammonium, but when the reaction was over, the catalyst, acetic acid, must be neutralized. In this step, the ammonium was turned into the tertiary amine when the potassium hydroxide methanol solution was added into the resulting mixture. At last the substances with low boiling point were removed by vacuum to obtain the resulting mixture. Comparing with the ammonium was transformed into the tertiary amine when the hydroxyl groups. In this step, it is possible that the tertiary amine would change into an ammonium, but when the reaction was over, the catalyst, acetic acid, must be neutralized. In this step, the ammonium was turned into the tertiary amine when the potassium hydroxide methanol solution was added into the resulting mixture. At last the substances with low boiling point were removed by vacuum to obtain the resulting mixture.

Spectral analysis, particle size of dispersions, molecular weight and mechanical properties of WBPU and WBPSU films

The structure of conventional WBPU and WBPSU films was identified using characteristic FT-IR peaks (Fig. 10). It can be seen from Fig. 10 a that there are strong absorption peaks at 3405, 2936, 2275 and 1714 cm$^{-1}$, which are ascribed to the vibration of $\text{–OH}$, $\text{–CH}_3$, $\text{–NCO}$ and $\text{C=O}$, respectively. After cross-linking (see Fig. 10 b), a new peak appeared at 3371 cm$^{-1}$, which was attributed to $\text{N–H}$ absorption. The $\text{–NCO}$ absorption peak at 2275 cm$^{-1}$ did not appear, perhaps indicating that the $\text{–NCO}$ group had reacted completely. The absorption peak at 1520 cm$^{-1}$ was attributed to $\text{N–H}$ bond vibration and $\text{C–N}$ symmetry stretch vibration. These indicated the presence of urethane bond formation. Also, three new peaks appeared at 839, 1050 and 1271 cm$^{-1}$ that were attributed to the $\text{Si–CH}_3$ and $\text{Si–O–R}$. In this report, PDMS was used with PEG, DMPA and HMDI and reacted to generate NCO-terminated prepolymers, followed by the processes of neutralization and dispersion to synthesize WBPSU dispersion. It is known that the properties of WBPU depend on starting materials used and their ratio,$[^{14,24}]$ The molar ratio of NCO/OH is 2.75 which were fixed for all the samples. The soft segment (polyol) content varied due to different polyol ratio of PDMS to PEG (see Table 1). The data in Table 1 showed that all dispersions were successfully prepared.

The mean particle size of all dispersions is shown in Table 2. Figure 11 confirms that the mean particle size varied slightly with respect to the ratio of PDMS to PEG. The PEG-based WBPU dispersion exhibited the smallest mean particle size among all of the dispersions. The mean particle size of any mixed polyol-based dispersions (WBPSU1–3) was larger than that of conventional WBPU. It was also observed that the mean particle size increased with increasing PDMS content. It has been shown elsewhere$[^{25}]$ that the macrodiol hydrophilicity can change the particle size of WBPU dispersion. The mean particle size increased with the presence of hydrophobic macrodiol.$[^{25}]$ This is well known that PDMS is more hydrophobic than PEG$[^{26}]$, thus the mean particle size increased with increasing PDMS content.

The molecular weight is considered to be one of the most important parameters of PU. The mechanical and adhesive properties are significantly affected by the molecular weight of PU.$[^{24,27}]$ The PU molecular weight depends on the polyol, chain extender and diisocyanate content.$[^{15,28}]$ According to Fig. 12, the conventional WBPU (PEG polyol based) exhibited the highest molecular weight among all of the samples. The mixed polyol-based WBPSU samples exhibited lower molecular weight than those for PEG-based PU (see Table 2). Moreover, the molecular

**Table 1. Composition of WBPU and WBPSU dispersions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>PEG</th>
<th>PDMS</th>
<th>HMDI</th>
<th>DMPA</th>
<th>TEA</th>
<th>PDMS/PEG</th>
<th>PDMS (Wt%)</th>
<th>PEG (Wt%)</th>
<th>Soft segment (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBPU</td>
<td>0.008</td>
<td>0.000</td>
<td>0.022</td>
<td>0.054</td>
<td>0.054</td>
<td>0.000</td>
<td>0.000</td>
<td>65.230</td>
<td>65.230</td>
</tr>
<tr>
<td>WBPSU1</td>
<td>0.007</td>
<td>0.001</td>
<td>0.022</td>
<td>0.054</td>
<td>0.054</td>
<td>0.142</td>
<td>2.090</td>
<td>60.840</td>
<td>62.930</td>
</tr>
<tr>
<td>WBPSU2</td>
<td>0.006</td>
<td>0.002</td>
<td>0.022</td>
<td>0.054</td>
<td>0.054</td>
<td>0.333</td>
<td>4.480</td>
<td>55.830</td>
<td>60.310</td>
</tr>
<tr>
<td>WBPSU3</td>
<td>0.003</td>
<td>0.005</td>
<td>0.022</td>
<td>0.054</td>
<td>0.054</td>
<td>1.667</td>
<td>14.230</td>
<td>35.420</td>
<td>49.650</td>
</tr>
</tbody>
</table>

Figure 9. $^{13}$C NMR spectrum of PDMS.

Figure 10. FT-IR spectra of (A) WBPU and (B) WBPSU films.


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weight gradually decreased with increasing PDMS content. As we decreased the PEG content using higher PDMS content of short chain length, the soft segment content decreased in WBPSU and thus decreased the molecular weight.[29]

The tensile strength, Young’s modulus and elongation at break (%) of all films are summarized in Table 2. All three of these properties depended on the polyl ratio. The PEG-based WBPU exhibited the maximum tensile strength and the Young’s modulus among all of the samples. The mixed polyl-based WBPSU had lower tensile strength, Young’s modulus and elongation at break (%) compared with those for conventional WBPU. All of these properties decreased with increasing PDMS content. However, above 4.480 wt% PDMS, the properties dropped sharply because the two polyols have significantly different polarity and may promote the phase separation that decreases the mechanical properties of polymer.[29] Therefore, a reasonable balance between the phase separation and interfacial adhesion is needed in order to achieve good mechanical properties in the WBPSU films.

AFM is a widely used technique to determine the surface topography of polymer films. Figure 13 shows the typical AFM topography of WBPU and the WBPSU3. The root mean square (RMS) roughness values are summarized in Table 2. The RMS value decreased with increasing PDMS content up to 14.230 wt %. The RMS values and images of all samples suggest that the WBPSU3 film is relatively smoother. This finding shows that silicone moieties enrich the surface of the coatings, rendering it more planar and smooth.

### Table 2. Particle size of dispersions, molecular weight, mechanical properties and RMS values of WBPU and WBPSU films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (nm)</th>
<th>Molecular weight (Mn)</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at Break (%)</th>
<th>RMS roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBPU</td>
<td>75</td>
<td>26000</td>
<td>5.500</td>
<td>34</td>
<td>718</td>
<td>0.870</td>
</tr>
<tr>
<td>WBPSU1</td>
<td>81</td>
<td>24000</td>
<td>5.300</td>
<td>33</td>
<td>712</td>
<td>0.710</td>
</tr>
<tr>
<td>WBPSU2</td>
<td>110</td>
<td>21000</td>
<td>4.400</td>
<td>24</td>
<td>673</td>
<td>0.360</td>
</tr>
<tr>
<td>WBPSU3</td>
<td>131</td>
<td>12000</td>
<td>1.100</td>
<td>7</td>
<td>162</td>
<td>0.159</td>
</tr>
</tbody>
</table>

**Figure 11.** Particle size of dispersions of (A) WBPU, (B) WBPSU1, (C) WBPSU2 and (D) WBPSU3 films.

**Figure 12.** Molecular weight measurements of (A) WBPU, (B) WBPSU1, (C) WBPSU2 and (D) WBPSU3 films.

**Figure 13.** AFM 3D topographs of (A) WBPU, (B) WBPSU2 (B), and (C) WBPSU3 films.
Seawater-immersion test

Seawater-immersion test of pure WBPU and WBPSU coatings were carried out to confirm the antifouling property depending on the PDMS contents. The antifouling, erosion and adhesion properties were examined by visual inspection. The fouled area (%) was also calculated using the image analysis software AxioVision Release 4.5 (Carl Zeiss). The pictures corresponding to 90 days of immersion are presented in Fig. 14, and all of the coatings were free from erosion. However, the coating using WBPSU3 (PDMS 14.230 wt%) started to slightly pull away from the PVC surface at third month. This might be due to the lower adhesive strength when using higher PDMS content.[30] The coating using WBPU was covered with various marine foulers including juvenile barnacles, oysters, polychaetes and a thin slime of an algal mat. Heavy macrofouling growth was also observed on this coating. On the other hand, the coatings using WBPSUs exhibited a decrease growth rate of marine fouling as the PDMS content increased. The lowest (almost free from fouling) marine fouling growth rate on coating was observed using 4.480 wt% PDMS (WBPSU2). Above 4.480 wt% PDMS, the marine fouling growth rate was almost constant. Unfortunately, the coating lost some mechanical strength at this stage, and thus the coating began to pull away from the PVC surface. The WBPSU1 contains lower PDMS content (2.090 wt%), and the surface is slightly silicone enriched; hence, this sample almost failed to combat against biofouling (see Fig. 14). However, with increasing PDMS content, lower biofouling was observed.[16,31] The WBPSU2 and WBPSU3 coatings were highly silicone enriched and made the coatings very smooth, and hence the samples were almost free from biofouling. The fouled area (%) of all coatings is summarized in Table 3. This value is almost 98% for WBPU after 90 days. In WBPSU coatings, the fouled area (%) decreased with inclusion of PDMS. Initially, the fouled area decreased slightly in WBPSU1 coatings. The fouled area (%) decreased dramatically for WBPSU2 and WBPSU3 coatings. This implies that after certain PDMS content is reached, the attachment of fouler on coating was very difficult due to very smooth surface, and it acted as a foul-release coating. In this study, the coatings were prepared using two different polyols. In WBPSU, the PDMS remained on the surface (contact with water) and the adhesive strength between the coating and PVC was controlled by the PEG and hard segment. The dual mechanism of this synthesized WBPSU made the resin very suitable for marine coating. The commercial marine paint mainly consists of polymer resins, pigments, additives and organic solvents. The examined coating consists of the synthesized waterborne polymer resins only. The WBPSU with optimum PDMS content (4.480 wt %) can be more effective with suitable pigments and additives to combat the marine fouling. The synthesized polymer resin mainly dispersed in water. When it will be coated on a ship hull only water will evaporate and can save the atmosphere from pollution. Thus, the system is fully environmentally friendly.[14] Investigations are ongoing in order to determine the long-term immersion behavior in sea water. The properties of the WBPSU resin can be adjusted by changing the various reactants and their ratio.

Water absorption ratio of the WBPU and WBPSU films

The water absorption ratio of the WBPU or WBPSU films is an important evidence of hydrophobicity. As shown in Fig. 15, the absorption ratio was greatly influenced by PDMS concentrations. With the increase of the silicone content, the water absorption ratio of the WBPU or WBPSU films decreased, which can be contributed to the excellent hydrophobicity of the PDMS monomer. When the silicone content increased from 0.000 to 0.005 mol l⁻¹, the water absorption of the films decreased sharply from 40 to

<table>
<thead>
<tr>
<th>Immersion days</th>
<th>WBPU</th>
<th>WBPSU1</th>
<th>WBPSU2</th>
<th>WBPSU3</th>
</tr>
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<tbody>
<tr>
<td>30</td>
<td>80</td>
<td>77</td>
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<td>90</td>
<td>98</td>
<td>98</td>
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<td>8</td>
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Figure 14. Photographs of all samples after immersion in sea water for 30 days (A), 60 days (B) and 90 days (C).
According to this figure, we conclude that an increase in PDMS concentration would give water resistance.

Thermal properties

The thermal properties of the WBPU and WBPSU films were evaluated by means of TGA and DSC under nitrogen atmosphere. The TGA curves of the copolymers are shown in Fig. 16 (a), WBPU and 16 (b) for WBPSU, respectively. The WBPU Fig. 16 (a) shows a stable situation up to 250°C. The chemical decomposition will start after this temperature, and the maximum decomposition is around 500°C. The same thermal behavior was obtained for (b) thermogram. From the comparison of TGA thermograms of (a) and (b), it can be concluded that the WBPSU is more stable than WBPU because char yield weight of WBPSU at 700°C was about 16% and in the case of (a) thermogram was about 3%. According to these results, it can be concluded that the modification of WBPU by silicone improved the thermal stability and increased the degradation temperature.

The DSC curves of the copolymers are shown in Fig. 17 (a and b) for WBPU and WBPSU, respectively. Figure 17 (a) reveals an endothermic shift around 18°C which corresponds to \( T_g \) of WBPU and \(-22.4\)°C for WBPSU. The peak position related to the glass transition temperature \( T_g \) was higher in the order WBPU > WBPSU. The glass transition temperature (\( T_g \)) values of WBPSU significantly decrease with siloxane loading due to the reduction in cohesive forces of attraction between polymer chains.\[32\] The reduction in cohesive forces between the polymer chains increased the mobility leading to a decrease in \( T_g \). There was little study about the thermal characterization of the WBPU and WBPSU films by DSC.

CONCLUSIONS

\( \alpha \)-Butyl \( \omega-N \)-N-dihydroxyethyl aminopropylpolydimethyldi-hydrosiloxane (PDMS), a monotelechelic polydimethyl-siloxane with a diol end group which can modify other organic polymers by graft copolymerization, can be prepared by hydroxyl protection, alkylation, hydrosilylation and deprotection. The successful synthesis of this kind of compound is a matter of primary importance for researches on graft copolymerization. On the other hand, WBPSU were successfully prepared with various compositions of PEG and silicone. The adequate balance of siloxane and PEG kept the mechanical strength and adhesive strength of the WBPSU coating adequate after 90 days of water exposure. A surface enriched in siloxane is not responsible for a smooth coating or the only reason for the observed good antifouling performance. It is more likely that the reason for good performance is because of other properties such as a combination of a low surface energy (caused by siloxane) and low modulus. The decrease in fouled area (%) implied that the growth of marine fouling decreased with increasing silicone content on WBPSU coatings. After 90 days, the fouled area was 98 and 6% for WBPU and WBPSU2, respectively. Thus, the synthesized WBPSU2 can be a good candidate for resolving the current scarcity of marine coating.

REFERENCES

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