

Article

The Synthesis of Nonionic Hyperbranched Organosilicone Surfactant and Characterization of Its Wetting Ability

Jie Liu ^{1,2}, Fei Fei Zhang ^{1,2,*}, Ying Hu Song ¹, Kun Lv ¹, Ni Zhang ³ and Yan Chun Li ^{1,2}

¹ School of Light Industry Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China; liujie@qlu.edu.cn (J.L.); songyinghu2020@163.com (Y.H.S.); 17861408040@163.com (K.L.); lyc@qlu.edu.cn (Y.C.L.)

² Key Laboratory for Green Technology of Leather Manufacture, China National Light Industry Council, Jinan 250353, China

³ College of Light Industry and Food Engineering, Guangxi University, Nanning 530000, China; 1816391040@st.gxu.edu.cn

* Correspondence: zffpg@qlu.edu.cn

Abstract: In this research, the epoxy silicone oil and self-made hydroxyl-terminated hyperbranched polymer (HBP-OH) were used to synthesis the nonionic hyperbranched organosilicone surfactant (NHSi). The molar rate of hydroxyl groups of HBP-OH and epoxy groups of epoxy silicon oil ($n_{\text{OH}}:n_{\text{epoxy}}$) was adjusted from 5:1~60:1 to prepare a series of NHSi. The Gel Permeation Chromatography (GPC), Fourier Transform Infrared Spectroscopy (FT-IR), contact angle measuring instrument, surface tensiometer and Scanning Electron Microscope (SEM) were employed to characterize the structure and property of HBP-OH and NHSi. GPC analysis indicated that the M_n of HBP-OH was 340.5. FT-IR analysis showed that with the increase of molar rate of $n_{\text{OH}}:n_{\text{epoxy}}$, the peak intensity of $-\text{OH}$ increased. The prepared NHSi was then used to prepare the water solution. The lowest surface tension of NHSi solution was $24.71 \text{ mN}\cdot\text{m}^{-1}$ when the $n_{\text{OH}}:n_{\text{epoxy}}$ was 30:1 in the preparation process. The minimum water contact angle of waterborne polyurethane (WPU) emulsion by adding 2% of NHSi was 14.85° on the surface of glass. The wetting experiments showed that the NHSi has good wetting ability to fixed sea-island superfine fiber synthetic material.

Keywords: hyperbranched; epoxy silicone; nonionic; wetting agent; superfine fiber



Citation: Liu, J.; Zhang, F.F.; Song, Y.H.; Lv, K.; Zhang, N.; Li, Y.C. The Synthesis of Nonionic Hyperbranched Organosilicone Surfactant and Characterization of Its Wetting Ability. *Coatings* **2021**, *11*, 32. <https://doi.org/10.3390/coatings11010032>

Received: 22 November 2020

Accepted: 28 December 2020

Published: 31 December 2020

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

A surfactant is a kind of molecule containing a hydrophilic segment and hydrophobic segment [1]. The adsorption of a surfactant on the solution surface, oil–water interface, or interface state and affect the interfacial properties, resulting in a series of important phenomena in application. Meanwhile, adding a small amount of surfactant into the solvent or solution can significantly reduce the surface or interfacial tension of the solution and make the surface or interface state of the system change obviously. The surfactant is widely used in textile, cosmetics, leather manufacture, synthetic material, and rubber industry because of its good wetting, dispersion, emulsion, permeation, and solubilizing abilities.

Wetting is the process of replacement of air by solution on the surface of material. A wetting agent is a kind of auxiliary which can increase this replacement ability [2–4]. Under the strategy of sustainable development in the whole world, the waterborne polyurethane (WPU) is gradually substituting the application of solvent-type polyurethane due to the unpleasant odor of dimethyl formamide (DMF) existed in the solvent-type polyurethane [5]. What's more, the working environment for solvent-type polyurethane manufacturing is not healthy for the operator. The continuous release of solvents will damage the natural environment and pose a threat to human health. Therefore, it is necessary to develop water-based materials, especially the WPU materials used in synthetic material industry and coating industry. Compared with a normal solvent-type dispersion system, the water

existed in a WPU system generally accounts for 60%~70% [6]. At room temperature, the surface tension of solvent is generally below 20~30 mN·m⁻¹, for example, the surface tension of acetone is 23.7 mN·m⁻¹, while that of water is 72.7 mN·m⁻¹. Therefore, the surface tension of the WPU emulsion was increased, and the spreading ability of WPU on the release paper and base are decreased. Accordingly, compared with the oil-based system, the wetting and spreading effect of WPU on the substrate is poor. The wetting agent used as the key matching auxiliary of water-based materials is the necessary part in the application of WPU.

Hyperbranched polymer has many advantages such as three-dimension structure, multi-terminal functional groups, and highly reaction activity [7]. In the past, the research of hyperbranched polymers was mainly focused on agriculture, medicine and cosmetics industry. In recent years, the application of hyperbranched polymers in surfactants [8] has gradually attracted many researchers' attention. The single-ended epoxy polydimethylsiloxane (SEPDMS) was grafted onto the hyperbranched polyamide by Wang Xuechuan to prepare a novel kind of surfactant PAMAM-Si [9]. It has good stability and emulsifying property. Furthermore, the dodecyl glycidyl ether (AGE) was used to modify the carboxyl-terminated dendrimer polymer (G₀ PAMAM-COOH) by Qin Yuanyuan to prepare a kind of dendrimer-linear structure surfactant [10]. The surface tension of the surfactant was 27.7 mN·m⁻¹ when the mass concentration of solution was 0.53 g/L. These two surfactants were both used in the leather fatliquoring process. It was reported that the mechanical properties and flexibility of leather were significantly increased due to the excellent emulsifying ability of these surfactants. The previous studies were mainly based on the amino and carboxyl terminated hyperbranched polymer [11]. When the synthetic surfactant is dissolved in water, the hydrophilic amino carboxyl groups in molecules will be ionized. The surface activity of these surfactants is easily affected by the pH and ionic strength of the solution [12,13]. While for the multi-hydroxyl nonionic type surfactant [14], the application condition is not too strict and can be widely used in many conditions. This research chooses the hydroxyl-terminated hyperbranched polymer (HBP-OH) and epoxy silicone oil as the raw materials to prepare a novel nonionic surfactant [15]. Furthermore, the application of hyperbranched structure surfactant in the WPU wetting field is explored. It will provide good suggestions for the application of hyperbranched surfactants in other fields. This kind of wetting agent may have better ability to reduce surface tension, and it can be used stably [16,17].

In this research, the hyperbranched structure was introduced into the preparation of surfactant. The nonionic surfactant was prepared by ring-opening reaction of epoxy silicone oil and grafting of HBP-OH. A series of nonionic hyperbranched surfactant (NHSi) were prepared by changing the molar rate of hydroxyl groups and epoxy groups. The change of HBP-OH dosage brings different mole fraction of hydrophilic silicone segment. Eventually, the wetting ability is variable according to the different ratio of hydrophilic segment and hydrophobic segment [18].

The wetting properties of NHSi were further studied in this paper. The surface tension of NHSi solution was measured by a specific surface area tensiometer. In order to evaluate the spreading ability of WPU, the contact angles of WPU emulsion on the surface of glass and silicone film with NHSi inside are determined. 5% NHSi solution was also used as the finishing agent to assess the wetting ability of NHSi to superfine fiber synthetic material. The aim of this study was to investigate whether the novel nonionic surfactants based on a hyperbranched structure is useful for the improvement of processing properties of WPU. This work is helpful to extend the application field of water-based coating materials on synthetic material or other substrates, and to solve the practical problems of wetting and spreading.

2. Experimental

2.1. Materials

Diethanolamine (DEA), trimethylolpropane (TMP), methyl acrylate (MA) and *p*-toluene sulphonic acid are analytical pure. They were purchased from Tianjin Damao chemical reagent factory of China (Tianjin, China); Boron trifluoride diethyl etherate, pyridine, isopropanol, acetic anhydride, acetonitrile, benzoic acid and phthalic anhydride are analytical pure. They were purchased from Tianjin Guangfu-chem. Ltd of China (Tianjin, China); Epoxy-silicone oil ($M_n = 4000$) was purchased from Iota Silicon Oil Co., Ltd of China (Anhui, China).

2.2. The Synthesis of NHSi

Quantitative analysis is very important in the synthesis of NHSi. The hydroxyl value of HBP-OH was determined by the PRC national standard GB12008.3-89 [19]. The hydroxyl value means the consumed quality (mg) of KOH by 1 g sample. The sample was esterified by acetic acid or phthalic anhydride firstly, then the KOH or NaOH was used to titrate the surplus acetic or phthalic anhydride. According to the consumed amount of acetic acid or phthalic anhydride in the sample, the hydroxyl value can be calculated.

Briefly, 100 mL pyridine and 15 mL acetic anhydride were added into clear brown bottle and mixed firstly. Then, 2 g HBP-OH (the accuracy was 1 mg) were added into two clean grinding mouth conical flasks of 100 mL. 10 mL acetic oxide-pyridine solution was transferred to the two conical flasks by pipette, separately. 2 mL pyridine was used to rinse the bottleneck. The other two conical flasks were prepared as the blank control group. 10 mL acetic oxide-pyridine solution was transferred to two flasks. Then, 2 mL pyridine was used to rinse the bottleneck, too. Then four flasks were equipped with reflux condensing tube. The samples were dissolved by shaking slowly. Then the mixture reacted for 1 h under 100 °C. Subsequently, 5 mL distilled water was added into the flask. After 10 min, the flasks were taken out and cooled to room temperature, and 5 drops of 0.1 mol/L phenolphthalein ethanol was added into the flask. Then, 1 mol/L NaOH solution was used to titrate the solution in the flasks. The hydroxyl value was calculated by Equation (1).

$$\text{hydroxyl value} = \frac{(V_0 - V) \times M \times 56.11}{W} \quad (1)$$

where, V_0 is the consumed KOH standard solution by blank control sample, mL; V is the consumed KOH standard solution by the samples, mL; M is the concentration of KOH standard solution, mol/L; W is the weight of sample, g.

The hydrochloric acid acetone method was used to determine the epoxy value of sample. After the epoxy group react with hydrochloric acid, the standard NaOH solution was used to titrate the excess hydrochloric acid. The acetone has good solubility to epoxy silicone, so the hydrochloric acid can react with epoxy group sufficiently.

The certain amount of epoxy silicone oil with accuracy of 0.001 g was added into 250 mL iodine number flasks. The pipette was used to transfer 25 mL hydrochloric acetone solution to the flasks, the flasks were then covered by lids and shaken to dissolve the silicone oil. The flasks were put in the shade place for 15 min. Then 5 drops of 1% phenolphthalein indicator were added into the flasks. The standard NaOH solution was used to titrate until the color of solution changed to pink. When the last drop was added into the system, the color of the solution didn't change in 30 s, when the titration destination was reached. Two parallel samples and blank control samples were weighted and tested. The epoxy value (EV) was determined by Equation (2).

$$EV = \frac{C(V_0 - V)}{m \times 10} \quad (2)$$

where, the EV represents the epoxy value of epoxy silicone, mol/100 g; C is the concentration of NaOH standard solution, mol/L; V_0 , V are the consumed volume of NaOH

standard solution by blank control sample and prepared sample, mL; M is the weight of sample, g.

The experiments results indicated that the hydroxyl value of HBP-OH was 198.82 mg NaOH/g. The epoxy value of epoxy silicone oil was 0.0376 mol/100 g.

The HBP-OH was synthesized as following: 0.1 mol DEA and 10 mL methyl alcohol were added into the three-necked flask [20]. The mixture was stirred until the DEA was dissolved. Then, 0.2 mol/L MA was added into the flask slowly. The temperature was raised to 35 °C to react for 4 h. The methyl alcohol and excess MA were removed by vacuum air-removed system. The transparent AB₂ type monomer oiliness material was obtained by this step. By controlling the molar rate of AB₂ monomer and center core, the TMP and *p*-toluene sulfonic acid were weighed and added into the flask firstly. Then the temperature was raised to 110~120 °C. The AB₂ monomer was added into the flask slowly. Then the reactant was transferred to the rotary evaporators to react until no bubble appeared.

Furthermore, to synthesis the NHSi, 10 g HBP-OH and 25 mL isopropanol were mixed in the beaker firstly. Then the mixture was added into the constant pressure drop funnel. The $n_{\text{OH}}:n_{\text{epoxy}}$ were preset to 60:1, 30:1, 20:1, 10:1, and 5:1. According to the hydroxyl value and epoxy value determination experimental results, the epoxy silicone oil was calculated by the preset molar ratio and weighed in the three-neck flask. Then 0.3%~0.5% boron trifluoride diethyl etherate which was used as the catalyzer and 10ml isopropanol were added into the three flasks together. Then the flask was set up in an oil bath pan and the temperature was raised to 110~130 °C. The constant pressure drop funnel was installed onto the three-neck flasks. The time of addition and reaction time was about 6 h. Then the product was transferred to pear-shaped parting funnel for separation and purification. 21 mL acetonitrile was added into the funnel. After slowly shaking, the funnel was fixed and stay for overnight. The next day, the sublayer NHSi was separated. Then, it was put into the oven for further drying. The synthesis route of NHSi was given in Figure 1.

2.3. Analysis and Measurement of NHSi Surfactant

The molecular weight of HBP-OH was analysis by SEC-MALS (Waters-e2695/Wyatt-Dawn Heleos II/ Wyatt Optilab, Santa Barbara, CA, USA), and the ultrapure water was used to prepare the NaNO₃ mobile phase with concentration of 0.1 mol/L [21]. The prepared mobile phase was filtered by 0.22 µm filter. The flow rate of mobile phase is 0.5 mL/min. The shodex 804 pillar was employed. The scope of separation was 500~4 × 10⁵. The HBP-OH sample with concentration of 0.5 mg/mL was prepared by the NaNO₃ mobile phase. Then the prepared sample was filtered by 0.22 µm filter, too.

The Fourier Transform Infrared Spectroscopy (FT-IR) (IR Prestige-21, Shimadzu, Japan) was employed to determine the molecular structure of NHSi. The contact angle tester (DSA25S, Kruss, Germany) was used to test the water contact angle of WPU. The NHSi was used to prepare a series solution with different mass concentration. A semi-automatic specific surface area tensiometer (BZY-48, Shanghai Hengping Instrument and Meter Factory, Shanghai, China) was used to test the surface tension of NHSi solution. The Scanning Electron Microscope (SEM) (Phenom pure plus, Phenom, Shanghai, China) was used to characterize the structure of fixed sea-island superfine synthetic material.

2.4. The Wetting Ability of NhsI to Superfine Fiber Synthetic Leather

Briefly, 5% NHSi solution was prepared to analysis the wetting ability of NHSi to superfine fiber synthetic material. The wetting states of superfine fiber synthetic material were recorded every 5 s compared with the blank control one. Compared with the unfigured sea-island fiber, the fixed sea-island superfine fiber possesses uniform fiber fineness [22]. In this research, in order to decrease the affection caused by the fiber differential, the fixed sea-island superfine fiber was chosen as the sample to testing the wetting ability of NHSi.

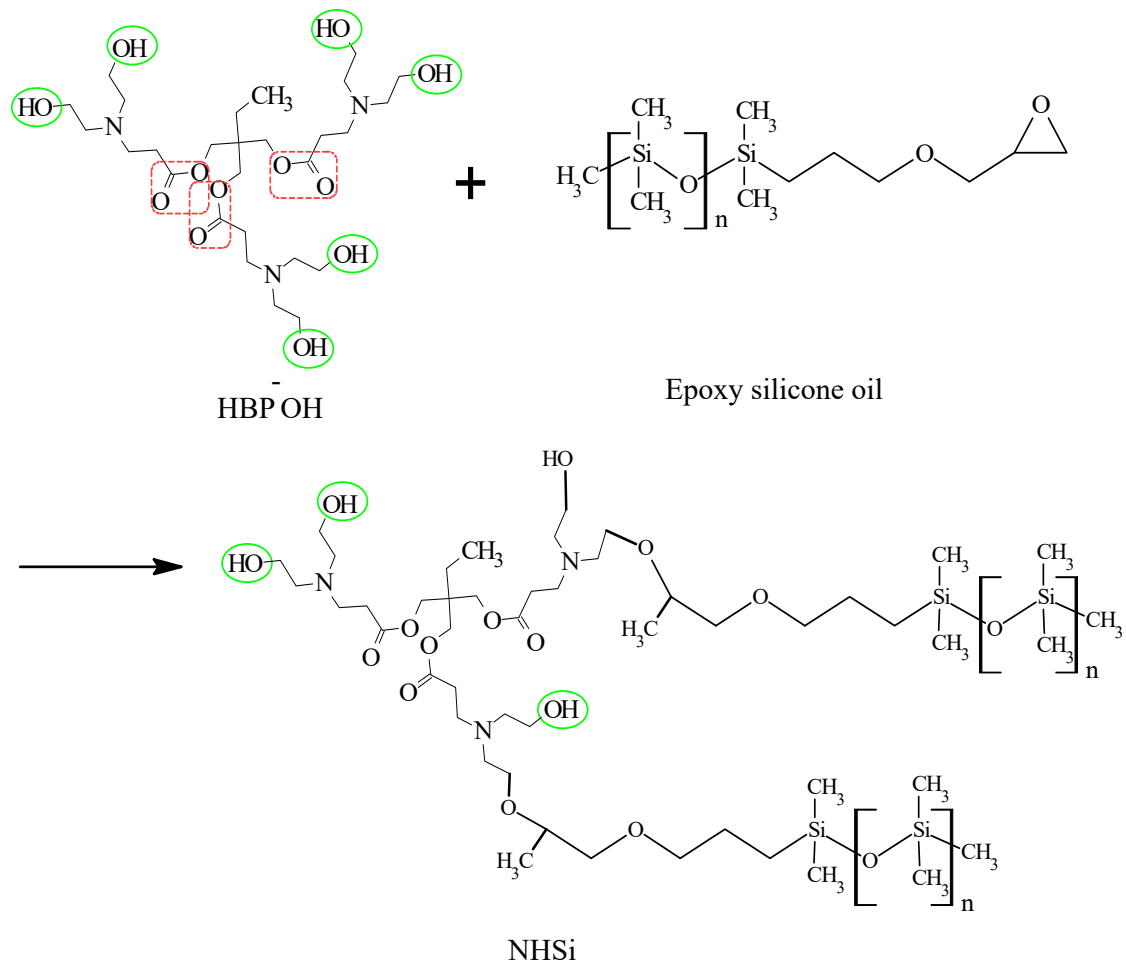


Figure 1. The synthesis route of NHSi.

3. Results and Discussion

3.1. GPC Analysis

The laser light scattering and differential detector was used to determine the specific refractive index increments dn/dc . The dn/dc of HBP-OH in dilute solution is measured off-line by the Optilab DSP. The dn/dc value was 0.1498. The GPC analysis results of HBP-OH was shown in Figure 2. The determined molecular weight of HBP-OH was shown in Table 1. The peaks at 340.5 and 372.7 were the main peaks, also some small peak appeared, too. So, some reactants were in the samples [23]. The M_n of HBP-OH were 340.5 and 372.7. The M_w of HBP-OH were 381.2 and 389.5. The hyperbranched polymer has more branching structure and smaller hydrodynamics volume [24]. So, the elution time is longer than the same molecular weight of linear structure. The analyzed molecular weight was smaller.

Table 1. The molecular weight and distribution of NHSi.

Molecular Weight	Peak 1	Peak 2
M_n , g/mol	340.5 (8.641%)	372.7 (7.01%)
M_w , g/mol	381.2 (9.296%)	389.5 (8.437%)
M_w/M_n	1.119 (12.692%)	1.045 (10.970%)

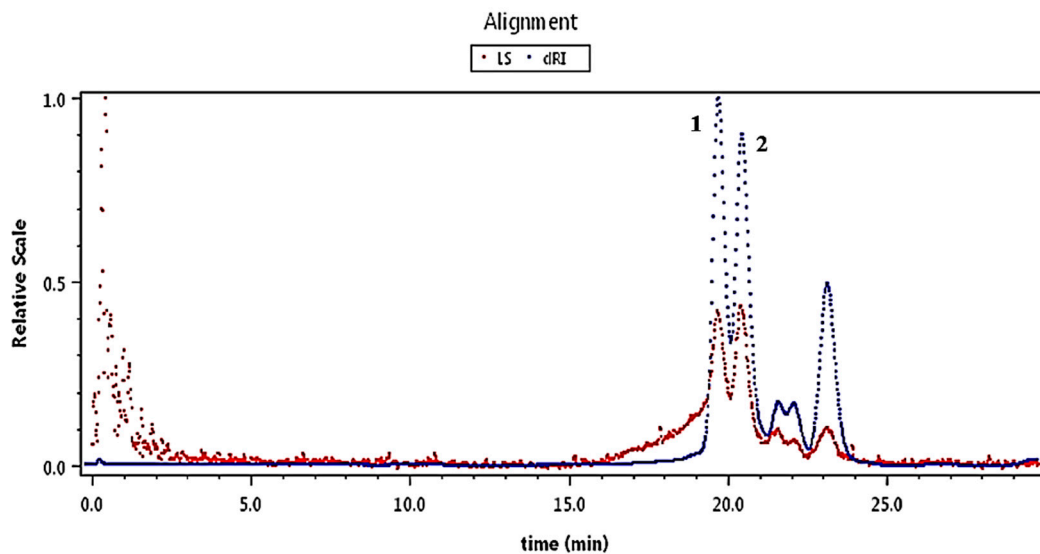


Figure 2. The analysis results of GPC.

Hanselmann proposed that the molecular distribution formula of hyperbranched polyester was $M_w/M_n = 1 + 1/f$ [25]. (f is functionality degree of nuclear monomer, the nuclear monomer TMP was 3 in this research). The M_w/M_n of HBP-OH was 1.119 and 1.045 ($1 + 1/f = 1.333$), which is close to the theoretical value.

The precision of the method related to the instrumentation and to sample preparation. Figure 3 shows the overlaid differential molar mass obtained using Zimm detector fit method [26]. The vertical coordinate was the linear differential molar mass. The peak area represents the content of a range of molar mass. According to Figure 3, the molar mass of HBP-OH centered on 0~400 g/mol.

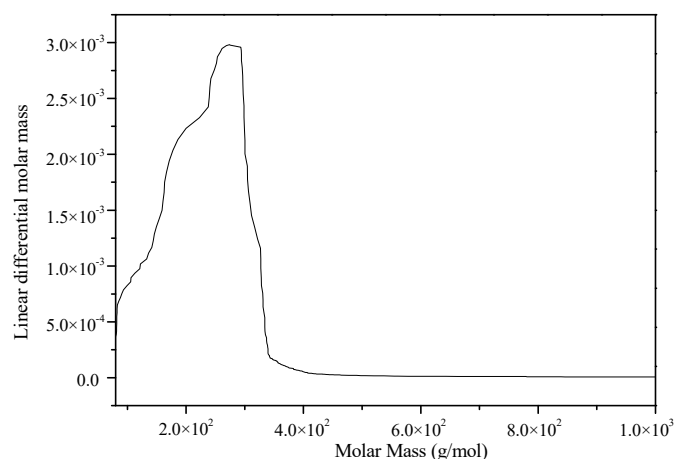


Figure 3. Overlaid differential molar mass of HBP-OH.

3.2. FT-IR

In order to analysis the chemical structures of raw materials and synthetic products, the FT-IR analysis results were shown in Figure 4. According to the FT-IR spectrum of HBP-OH in Figure 4a, the stretching vibration peak of hydroxyl group of HBP-OH was displayed in 3398 cm^{-1} [27]. The absorption peak of ester group was shown in 1714 cm^{-1} . The absorption peaks of secondary amine and tertiary amine of HBP-OH were shown in 1621 and 1043 cm^{-1} [20]. The FT-IR spectrum of epoxy silicone oil was shown in Figure 4b. The peak at 1089 cm^{-1} belonged to stretching vibration peak of Si-O-Si, and the peak

at 1255 cm^{-1} can be ascribed to the bending absorption peak of C–H bond on methyl group connected with silicon atom. The band at 802 cm^{-1} corresponds to the characteristic absorption peaks of epoxy groups [9].

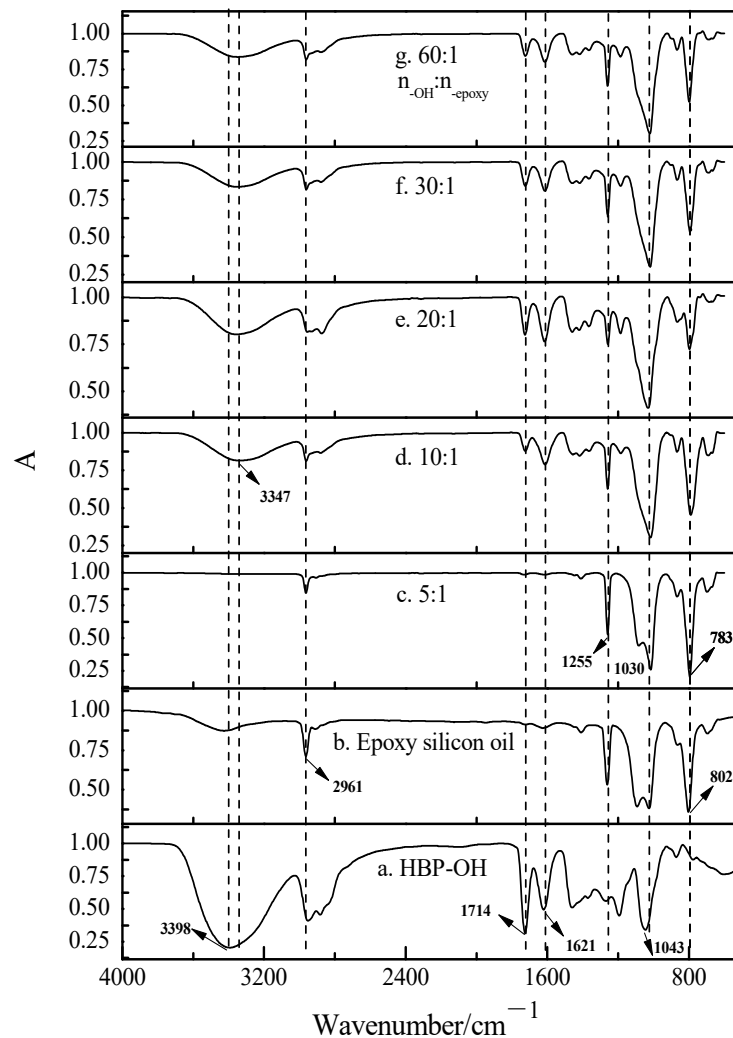


Figure 4. FT-IR spectrum of raw materials and NHSi with different reaction ratio of $n\text{-OH}:n\text{-epoxy}$. (a) HBP-OH, (b) Epoxy silicon oil, (c) 5:1, (d) 10:1, (e) 20:1, (f) 30:1, (g) 60:1.

The FT-IR spectrums of NHSi synthesized by different molar ratio were shown in Figure 4c–g. The terminated hydroxyl group and epoxy silicone oil reacted with each other by ring opening reaction of epoxy group and generated the ether groups. The stretching vibration of ether group was observed around 1030 cm^{-1} . Compare the spectrum of c, d, e, f, and g in Figure 4, the peak intensity at 1255 cm^{-1} decreased, which means that the ratio of Si–C decreased. It is attributed to the decrease of organosilicon components in the product molecules chain with the increase of HBP-OH [28]. Furthermore, with the increase of the molar ratio, the stretching vibration peak of –OH was red shifted from 3398 to 3347 cm^{-1} , suggesting that the association of hydrogen bond owing to the increase of –OH content ratio in the structure.

3.3. The Determination of Contact Angle

Briefly, 2% NHSi was added into 30 g WPU to prepare the WPU sizing. The contact angle of WPU sizing on the surface of glass and pellosil were tested. The contact angles results were shown in Figure 5. It can be seen from the figure that the WPU sizing with

NHSi has different surface tension. In particular, the minimum water contact angle was obtained when the $-n_{OH}:-n_{epoxy}$ was 30:1. The contact angle were 14.85° and 64.78° on the surface of glass and pellosil, indicating that the NHSi possesses excellent wettability. When the WPU sizing is coated on the surface of the substrate, a part of the NHSi is at the bottom of the coating, and it contacts with the wetted surface. The lipophilic segment like siloxane fragment is adsorbed on the solid surface, and the hydrophilic group extends outward to the water [29]. The contact between water and substrate was changed to the contact between water and hydrophilic group of NHSi, and a sandwich structure with surfactant as intermediate layer is formed [30]. This makes the water phase spread more easily, to achieve the purpose of wetting. As for the same WPU sizing, the contact angle on the glass is much smaller than that on the pellosil. Because the surface energy of the pellosil is lower and it's difficult to be wetted by the liquid. The surfactants with different molar ratio of hydroxyl group and epoxy group have different wettability. However, it does not simply show the corresponding change trend. It is suggested that the wettability of the surfactants modified by hydroxyl terminated hyperbranched polymers is not only related to the ratio of hydrophilic and hydrophobic groups.

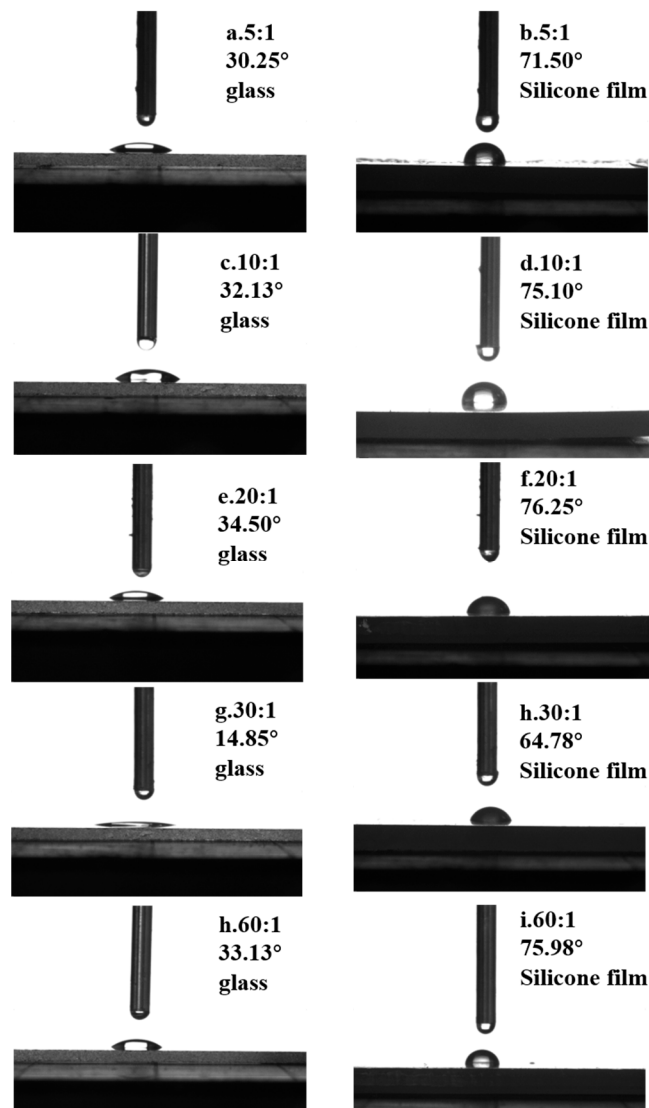


Figure 5. The results of determination of contact angle.

3.4. The Determination of Surface Tension of NHSi

The surface tension curves [18] of NHSi prepared by different molar ratio ($n_{\text{OH}}:n_{\text{epoxy}}$) were shown in Figure 6. It can be seen from Figure 6 that the surface tension of NHSi solution decreased with the increase of solution concentration, but the decreasing trend becomes slower after reaching a certain concentration. When the ratio of $n_{\text{OH}}:n_{\text{epoxy}}$ was 30:1, the lowest surface tension $24.71 \text{ mN}\cdot\text{m}^{-1}$ was obtained when the mass concentration was 5 g/L. When NHSi was dissolved in water, the hydrophilic segment (hydroxyl groups) was switched to the inner part of aqueous solution, while the organosilicone linear segment was spread on the surface of water. The hyperbranched structure decreases the distance between the adjacent surfactants polymer [31], and the attraction force between surfactant is lower than the hydrone molecule. The surface tension of NHSi solution decreased.

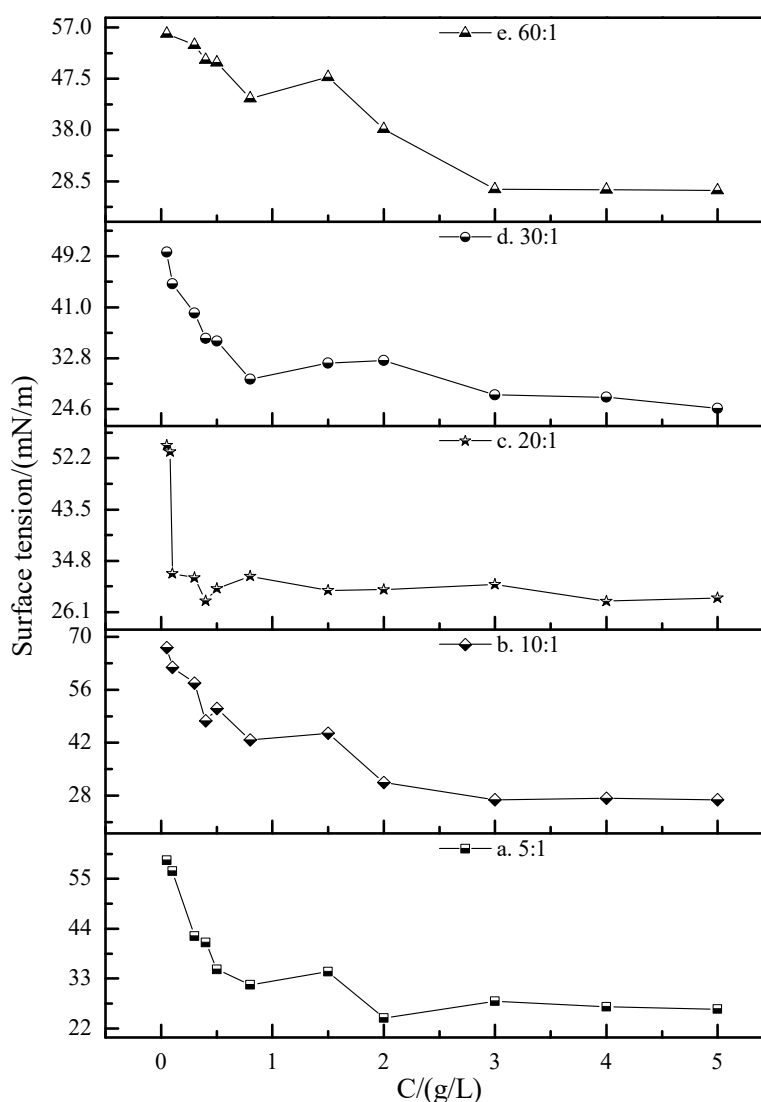


Figure 6. The surface tension of NHSi with different $n_{\text{OH}}:n_{\text{epoxy}}$.

3.5. The Wetting Ability of NHSi to Superfine Fiber Synthetic Material

The wetting agent is a kind of auxiliaries which can promote the wetting process of fiber or fabric by water quickly, and then penetrate to the inner part of the fiber. Positive ion surfactant is not suitable for the wetting agent, because they will be attracted by fiber and impede the wetting process. The major type is nonionic and negative ion surfactant. The NHSi is a kind of nonionic surfactant due to the existence of hydroxyl groups. So, it

has good penetration property. The fixed sea-island superfine fiber is a kind of modern base material used in synthetic material industry. The nonwoven material with sea-island structure will be dipped in polyurethane sizing to become a composite material. Through alkali decrement, the “sea” part was hydrolyzed, and the “island” part appears. The diameter of single fiber was about 0.1dtex. So, the specific surface area of superfine fiber synthetic material is very large. The SEM pictures of the surface and the cross section of fixed sea-island superfine fiber synthetic material were shown in Figure 7. In Figure 7a, most fibers exist in bundles. However, the fineness of fiber is very small and homogeneous (Figure 7b). When it was dipped in water, the wetting process is slow due to its big specific surface area.

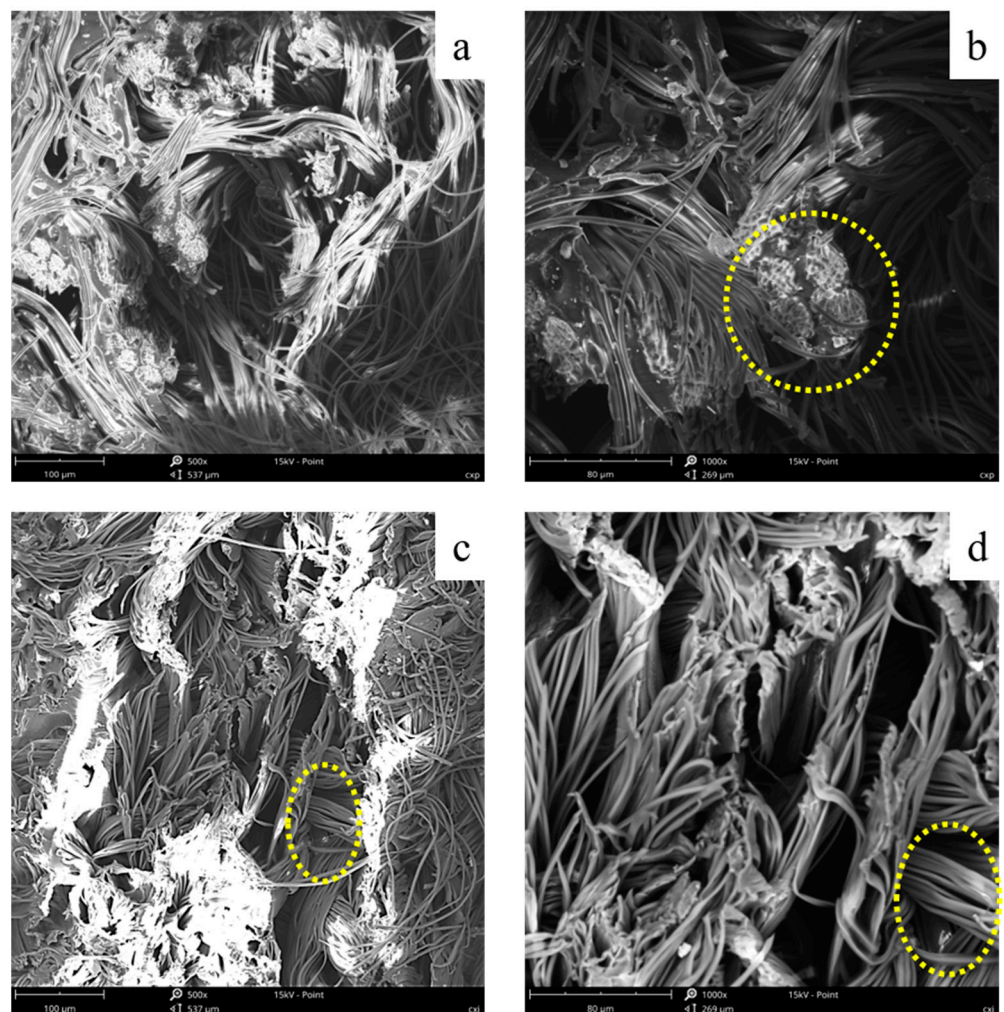


Figure 7. The structures of superfine fiber synthetic material (a), the surface of fixed sea-island superfine fiber, $\times 500$; (b), the surface of fixed sea-island superfine fiber, $\times 1000$; (c), the cross section of fixed sea-island superfine fiber, $\times 500$; (d) the cross section of fixed sea-island superfine fiber, $\times 1000$.

Two pieces of fixed sea-island superfine fiber synthetic material were cut into the size of $5 \times 5 \text{ cm}^2$. They were put into 100 g water. Sample 1 was blank control aqueous solution. 5% NHSi solution was prepared and marked as sample 2. Figure 8 shows the wetting results of the superfine fiber synthetic material. The superfine synthetic material was fully wetted in 10 s in sample 2, while for the blank aqueous solution, the superfine synthetic material was fully wetted after 25 s. Hence, the branched molecule with $-\text{OH}$ groups endows the fiber with good hydrophilic properties [32]. And the wetting process

was accelerated by NHSi. Meantime, the existence of Si–O chain in the NHSi molecular makes the fibers more flexible.

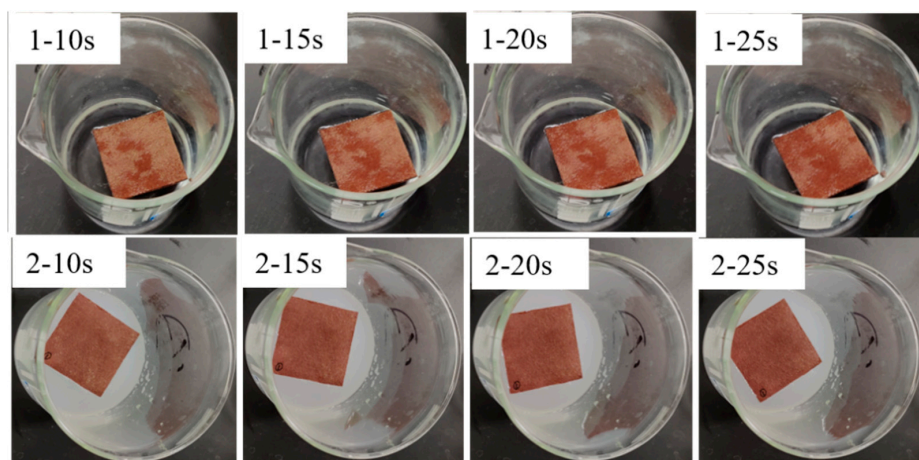


Figure 8. The wetting state of superfine fiber synthetic material (1, blank aqueous solution; 2, 5% NHSi wetting agent solution).

4. Conclusions

Nonionic hyperbranched organosilicon surfactants were prepared by using HBP-OH and epoxy silicone oil as raw materials and the boron trifluoride ether as the catalyst. Ring opening reactions involved in the study was carried out at 110~130 °C for 6 h. A series of NHSi were synthesized by changing the molar ratio of hydroxyl group and epoxy group, and their surface activity was tested. When the value is 30:1, the prepared NHSi has excellent surface properties. If NHSi concentration is 5 g/L, the surface tension is as low as 24.71 mN·m⁻¹, indicating that a hyperbranched structure can effectively reduce the surface attraction of an aqueous solution and improve its wettability to the substrate. Further application experiments show that the water contact angle of the WPU sizing with NHSi was only 14.85° on the glass surface, and the aqueous solution with a small amount of NHSi also has good wettability for the fixed sea-island superfine fiber synthetic material. The content presented in this paper is only a part of our study. In addition to wettability, NHSi also has in-depth influence on other functional properties of waterborne coatings. For example, it is found that WPU film with NHSi has certain anti-graffiti property. Relevant research is in progress and will be reported in the following research.

Author Contributions: Methodology, J.L. and F.F.Z.; Investigation, F.F.Z., N.Z., Y.H.S., and K.L.; Writing—Review & Editing, J.C.L. and F.F.Z.; Funding acquisition, J.L., F.F.Z., and Y.C.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Key R&D Plan of the 13th Five Year Plan (CN) [grant numbers 2017YFB0308600]; the Science and Technology Program of Colleges and Universities in Shandong Province (CN) [grant numbers J18KA114].

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Shaban, S.M.; Kang, J.; Kim, D.H. Surfactants: Recent advances and their applications. *Compos. Commun.* **2020**, *22*, 100537. [[CrossRef](#)]
- Rosen, M.J.; Kunjappu, J.T. *Surfactants and Interfacial Phenomena*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2010; pp. 182–183.
- Barz, J.; Haupt, M.; Oehr, C.; Hirth, T.; Grimmer, P. Stability and water wetting behavior of superhydrophobic polyurethane films created by hot embossing and plasma etching and coating. *Plasma Process. Polym.* **2019**, *16*, 1800214. [[CrossRef](#)]

4. Huang, Y.; Guo, M.D.; Tan, J.L.; Feng, S.Y. Impact of molecular architecture on surface properties and aqueous stabilities of silicone-based carboxylate surfactants. *Langmuir* **2020**, *36*, 2023–2029. [[CrossRef](#)]
5. Dai, M.W.; Wang, J.Y.; Zhang, Y. Improving water resistance of waterborne polyurethane coating with high transparency and good mechanical properties. *Colloid. Surf. A* **2020**, *601*, 124994. [[CrossRef](#)]
6. Yang, F.; Wu, Y.; Zhang, S.Q.; Zhang, H.M.; Zhao, S.L.; Zhang, J.L.; Fei, B.H. Mechanical and thermal properties of waterborne polyurethane coating modified through one-step cellulose nanocrystals/graphene materials sols method. *Coatings* **2020**, *10*, 40. [[CrossRef](#)]
7. Archer, R.J.; Nienhaus, B.B.; Dunderdale, G.J.; Hozumi, A. Recent progress and future directions of multifunctional (super)wetting smooth/structured. *Adv. Funct. Mater.* **2020**, *30*, 1907772. [[CrossRef](#)]
8. Băran, A.; Iovescu, A.; Gosecka, M.; Sfîngă, G.; Peretz, S.; Basinska, T.; Slomkowski, S.; Maxim, M.E.; Anghel, D.F. Peculiarities of linear and hyperbranched polyglycidols in water and aqueous surfactant solutions. *Eur. Polym. J.* **2017**, *94*, 162–172. [[CrossRef](#)]
9. Wang, X.C.; Sun, S.W.; Wang, H.J.; Guo, X.X. Synthesis and characterization of polysiloxane grafted polyamide-amine surfactants. *J. Surfactants Deterg.* **2017**, *20*, 521–528. [[CrossRef](#)]
10. Wang, X.C.; Qin, Y.Y.; Wang, H.J. Synthesis and characterization of dendritic-linear poly(amido) amine. *Polym. Mater. Sci. Eng.* **2015**, *31*, 41–45.
11. Riascos, I.M.; Hoyos, B.A. Fluorocarbon Versus Hydrocarbon Organosilicon Surfactants for Wettability Alteration: A Molecular Dynamics Approach. *J. Ind. Eng. Chem.* **2020**, *88*, 224–232. [[CrossRef](#)]
12. Bi, Z.C.; Liao, W.S.; Qi, L.Y. Synthesis and wetting properties of a novel wetting agent by molecular design process. *Colloid Surf. A* **2005**, *256*, 117–121. [[CrossRef](#)]
13. Mestri, R.S.; Pratap, A.P.; Panchal, K.H.; Gamot, K.; Datir, K.A. Synthesis of cleavable silicone surfactant for water-repellent application. *Chem. Pap.* **2020**, *74*, 1407–1416. [[CrossRef](#)]
14. Andrade, B.; Knewstubb, S.N.; Harris, K.; Tucker, C.J.; Katz, J.S.; Zimmerman, S.C. Nonionic Surfactant Properties of Amphiphilic Hyperbranched Polyglycerols. *Langmuir* **2020**, *36*, 10103–10109. [[CrossRef](#)]
15. Pukale, D.D.; Bansode, A.S.; Jadhav, N.L.; Pinjari, D.V.; Kulkarni, R.R. Review on silicone surfactants: Silicone-based gemini surfactants, physicochemical properties and applications. *Tenside Surfactants Det.* **2019**, *56*, 268–278. [[CrossRef](#)]
16. Gao, Y.; Lu, J.J.; Zhang, P.J.; Shi, G.C.; Li, Y.; Zhao, J.Y.; Liu, Z.F.; Yang, J.; Du, F.P.; Fan, R.J. Wetting and adhesion behavior on apple tree leaf surface by adding different surfactants. *Colloids Surf. B* **2020**, *187*, 110602. [[CrossRef](#)]
17. Ohno, M.; Esumi, K.; Meguro, K. Aqueous Solution Properties of a Silicone Surfactant and Its Mixed Surfactant Systems. *J. Oil Chem. Soc.* **1992**, *69*, 80–84. [[CrossRef](#)]
18. Varaprasad, N.S.S.; Ramakrishnan, S. Hybrasurfs. A New Class of Hyperbranched Surfactants. *Langmuir* **2018**, *34*, 11464–11472. [[CrossRef](#)]
19. *Polyether Polyols-Determination of Hydroxyl Number*; GB 12008.3-89; State Bureau of Technical Supervision: Shenzhen, China, 1990.
20. Wang, X.C.; Yuan, X.Z.; Qiang, T.T.; Chen, X. Synthesis of hydroxyl-terminated hyperbranched polymer and its influences retannage properties of chrome tanned leather. *Fine Chem.* **2009**, *26*, 68–72.
21. Matsuda, Y.; Kobayashi, M.; Takahara, A.; Tanaka, A.; Sato, T. On the dimension of a hyperbranched polymer synthesized from a styrene derivative. *Polym. J.* **2008**, *40*, 375–378. [[CrossRef](#)]
22. Yang, H.Y.; Zhai, L.S.; Li, K.; Liu, X.; Deng, B.; Xu, W.L. A highly efficient nano-graphite-doped TiO₂ photocatalyst with a unique sea-island structure for visible-light degradation. *Catal. Sci. Technol.* **2020**, *10*, 1161–1170. [[CrossRef](#)]
23. Ren, L.F.; Niu, Q.X.; Zhao, J.; Qiang, T.T. Amphiphilic hyperbranched polymers: Synthesis, characterization and self-assembly performance. *J. Leather Sci. Eng.* **2020**, *2*, 4–16. [[CrossRef](#)]
24. Feng, Q.; Liu, H.; Peng, Z.G.; Zheng, Y. Synthesis, Characterization and evaluation of long-acting hyperbranched cationic polymer clay stabilizer used in water flooding. *Polym. Test.* **2020**, *82*, 106344. [[CrossRef](#)]
25. Sunder, A.; Hanselmann, R.; Frey, H.; Mulhaupt, R. Controlled synthesis of hyperbranched polyglycerols by ring-opening multibranching polymerization. *Macromolecules* **1999**, *32*, 4240–4246. [[CrossRef](#)]
26. Zhang, G.P.; Li, J.Q.; Sun, S.X.; Luo, Y.J. Azido-terminated hyperbranched multi-arm copolymer as energetic macromolecular plasticizer. *Propellants Explos. Pyrotech.* **2019**, *44*, 345–354. [[CrossRef](#)]
27. Wang, F.; Liu, L.Z.; Zhang, X.R.; Weng, L. Hyperbranched unsaturated polyester resin for application in impregnation coatings. *Iran. Polym. J.* **2017**, *26*, 81–89. [[CrossRef](#)]
28. Chozhan, C.K.; Chandramohan, A.; Alagar, M. Benzoxazine modified diglycidyl ether of bisphenol-a/silicon/siliconized epoxy hybrid polymer matrices: Mechanical, thermal, electrical and morphological properties. *J. Macromol. Sci. A* **2019**, *56*, 1–17. [[CrossRef](#)]
29. Wang, H.; Wang, C.Q.; Fu, J.G.; Gu, G.H. Wetting behavior and mechanism of wetting agents on low-energy. *Colloid Surf. A* **2013**, *424*, 10–17. [[CrossRef](#)]
30. Pukale, D.D.; Bansode, A.S.; Pinjari, D.V.; Kulkarni, R.R.; Sayed, U. Application of silicone surfactant along with hydrocarbon surfactants to textile washing for the removal of different complex stains. *J. Surfactants Deterg.* **2017**, *20*, 287–295. [[CrossRef](#)]
31. Li, Z.H. *Synthesis and Properties of Betaine Zwitterionic Surfactants with Branched Structure*; Dalian University of Technology: Dalian, China, 2013.
32. Mit-Uppatham, C.; Nithitanakul, M.; Supaphol, P. Ultrafine electrospun polyamide-6 fibers: Effect of solution conditions on morphology and average fiber diameter. *Macromol. Chem. Phys.* **2004**, *205*, 2327–2338. [[CrossRef](#)]