Preparation and Characterization of a Hyperbranched Polyethoxysiloxane Based Anti-fouling Coating

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ABSTRACT: A hyperbranched polyethoxysiloxane was synthesized via hydrolytic polycondensation between methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS), with hydrochloride acid as catalyst. FTIR, ^{1}H NMR, ^{29}Si NMR, and GPC measurements confirmed that the polyethoxysiloxane synthesized was indeed a hyperbranched polymer with a degree of branching of 0.67. It was also found that there were no silanol groups in polymer matrix. This quality can effectively enhance its storage stability. Based on the hyperbranched polyethoxysiloxane, a novel antifouling coating with high curing speed at ambient temperature was developed. The recipe and other technique parameters of the coating were revealed and investigated. Experiments indicate that the coating performs well as an antifouling agent and can be applied to various ceramic products. By using scanning electron microscope (SEM) to inspect the surface of a polished tile applied with the coating, the antifouling mechanism was studied and the results were explained in accordance with the penetrating and crosslinking of the macromolecules of hyperbrached polyethoxysiloxane into the microdefects on the surface of tiles. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5818–5824, 2006

Key words: hyperbranched; polyethoxysiloxane; antifouling coating

INTRODUCTION

Highly branched polymers are attracting great attentions from polymer scientists recently due to their special molecular architectures, distinct physical properties, and potential industrial applications. Highly branched polymers can be classified into dendrimers and hyperbranched polymers depending on their different molecular morphologies.[1,2] Dendrimers, having highly regular structures and well-controlled molecular weights, are usually synthesized by multistep reactions with tedious isolation and purification procedures. On the other hand, compared to dendrimers, hyperbranched polymers having less perfect molecular structures can be synthesized via a single-step polymerization from AB$_x$-type monomers. Obviously, due to the simple preparation and the simple method of purification, hyperbranched polymers could be easily manufactured on a large scale, and as a result, leading to wide applications in the near future.[3–7]

Many organosilicon-based hyperbranched polymers with different end functional groups such as vinyl,[8] allyl,[9] and silicon hydride groups[10–12] can be synthesized via hydrosilylation of AB$_x$ monomers ($x \geq 2$), where A and B usually represent unsaturated and silicon hydride groups, respectively. Besides, there is another AB$_x$ monomer system being worth mentioning, where A represents a silanol group, which not only can react with B groups, but also can react with itself, and B represents alkoxy silane group, which can react with only a silanol group.[13] For this system, the controlling of silanol self-condensation during polymerization should be a key factor to obtain a qualified hyperbranched polymer.[3] In recent years, the syntheses of hyperbranched polyalkoxysilioxanes via the condensation of different AB$_x$-type monomers have been developed rapidly. With improved technology, many organosilicon-based hyperbranched polymers possessing well-controlled molecular mass, desired degree of branching (DB), good chemical stability, and excellent physical properties have been synthesized.[13]

In this paper, we reported a preparation strategy of a novel hyperbranched polyethoxysiloxane using a hydrolytic product of tetraethoxysilane (TEOS) as a core, and then stepwise addition of methyltriethoxysilane (MTES) to initiate polycondensation. Based on hyperbranched polyethoxysiloxane's distinct physical properties including low surface energy, low viscosity, high fluidity, and chemical reactivity, a coating with high curing speed at ambient temperature and

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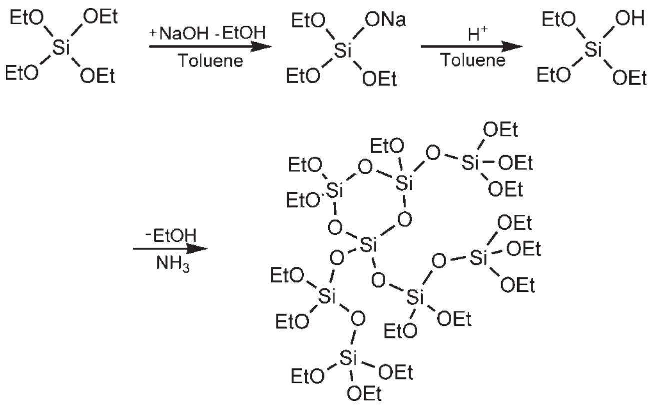


Scheme 1 The chemical routes for synthesis of polyethoxysiloxane via polycondensation of silanol groups.

an excellent antifouling property for tiles was developed. By using SEM technology and contact angle measurements, the antifouling mechanism of coating was studied and discussed in accordance with macromolecule's penetrating and crosslinking into microdefects on the surface of tile.

EXPERIMENTAL

Materials

MTES (98% pure, industrial grade) was purchased from Bengbu Company of Organosilicon Chemistry (China). TEOS (reagent grade) was obtained from Tianjin Chemical Reagent (China). Hydrochloric acid (HCl, 48%, analytical grade) was obtained from Xi'an Chemical Agent (China). Dibutyltin dilaurate (DBTDL, analytical grade) was supplied by Shanpu Chemical and Technological Ltd. (China). Other solvents and reagents were all analytical grade, and used as received without further purification.

Synthesis

TEOS (4.0 g; 0.019 mol) was charged into a 100-mL three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel. A mixture of 0.1 g of hydrochloric acid (HCl 48%) and 1.0 g of distilled water was added dropwise with stirring. The system was first stirred for 30 min at ambient temperature and heated to 50°C for another 30 min. Then, after it was cooled to 35°C, 8.0 g of MTES together with 1.0 g of distilled water was added dropwise for 30 min. The mixture was allowed to react for 30 min, and then, another portion of MTES (8.0 g) was added. The system was continuously heated to 60°C under stirring for 60 min and then cooled down to ambient temperature. About 0.5 g of sodium carbonate was added to neutralize the system. After filtration, a colorless liquid was obtained, labeled as HBPESS.

HBPESS was distilled under vacuum (−0.1 MPa) and then dried at 60°C for 48 h. Hyperbranched polyethoxysiloxane was finally obtained as a colorless viscous liquid.

Instrumental analyses

Fourier transform infrared (FTIR) spectra were recorded on a Specode WQF-310 model (Rui-Li Corp., Beijing, China), using KBr disk as the sample holder. The transmission mode was used and the measuring time was 300 s. The wave number range was set from 4000 to 400 cm^{-1}.

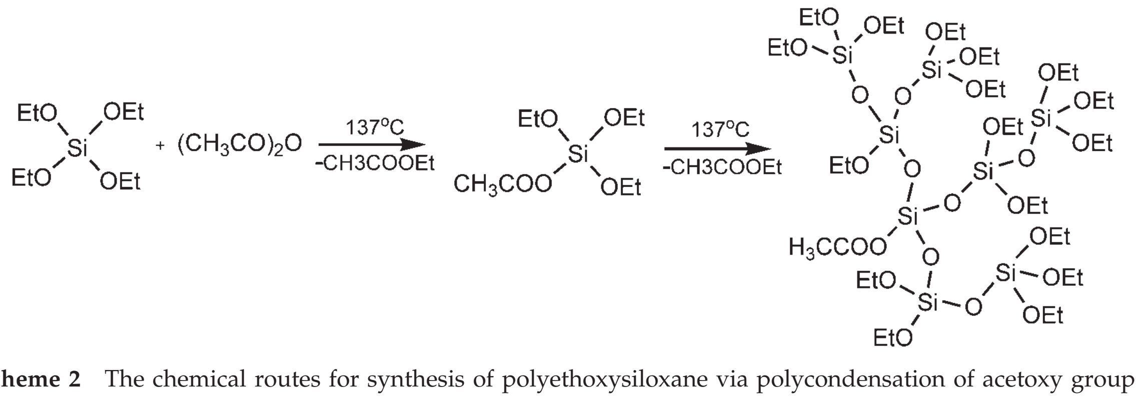
^{1}H NMR and ^{29}Si NMR measurements were performed on Bruker DMX 300 spectrometer at room temperature, using $CDCl_3$ as solvent, tetramethylsilane (TMS) as an internal standard (0 ppm), and quartz tube as sample holder.

The surface images of the tile before and after being applied with coating were inspected using a scanning electron microscope of AMRAY 1000B model. Its accelerating voltage was about 20 kV.

Contact angle was determined on a JY-82 Goniometer (Beijing, China) at room temperature.

Luster degree was measured on a KCS-1A Luster Degree Tester (Shanghai, China) at room temperature.

The weight average molecular weight and polydispersity index were measured with a Waters 600 model instrument at room temperature, using THF as the



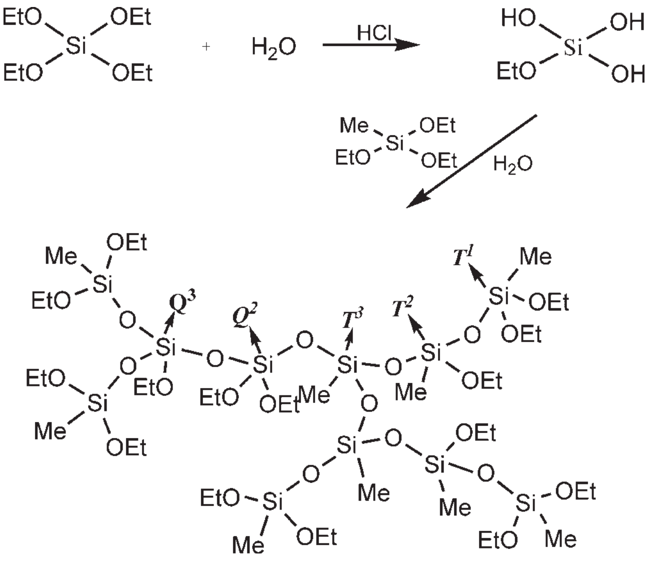
Scheme 2 The chemical routes for synthesis of polyethoxysiloxane via polycondensation of acetoxy groups.

mobile phase with a flow rate of 1.0 mL/min. Two 5 μm PL gel columns (Polymer Laboratories, UK) were cascade-connected for conducting sample separation. The molecular weights were calculated using monodispersity polystyrene as the standards.

RESULTS AND DISCUSSION

Synthesis of hyperbranched polyethoxylsiloxane

Hyperbranched polyethoxysiloxane can be synthesized via hydrolytic polycondensation of TEOS under acidic condition.[14] This chemical route is simple, convenient, and suitable for industrial production. However, if all reactants are added at once, the product obtained may still carry a small portion of silanol groups even if the reaction time is prolonged.[15] These silanol groups can gradually undergo further condensation and even crosslinking with those unhydrolytic ethoxysiloxane groups or with themselves. As a result, this can cause gelation of the product during storage.[16] Jaumann[13] reported that hyperbranched polyethoxysiloxanes containing no silanol groups can be synthesized via self-condensation of triethoxysilanol or self-condensation of acetoxytriethoxysilane as shown in Schemes 1 and 2, respectively. However, in Scheme 1, as additional organic solvents should be added during synthesis, the purification of the final product may not only cause pollution problems but also make the process more complicated and inconvenient. Besides, it is difficult to control the exact degree of hydrolysis by this chemical route. The disadvantage of the synthetic stratagem shown in Scheme 2 is that the reaction must be conducted at a higher temperature because of low reactivity of reactants used.



Scheme 3 The chemical routes of polyethoxylsiloxane via polycondensation of TEOS and MTES.

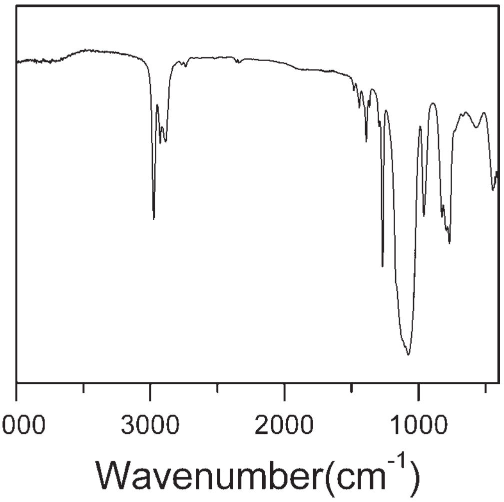


Figure 1 FTIR spectrum of hyperbranched polyethoxysiloxane.

In this research, TEOS is used as a starting monomer and its hydrolytic product can further react with MTES. By the end of polycondensation reaction, MTES can also play a role as a terminal agent. Thus, a hyperbranched polyethoxysiloxane without silanol groups can be synthesized via a simple and convenient chemical route as presented in Scheme 3. However, during synthesis, three important factors must be strictly controlled: catalyst content, amount of water, and monomer feeding procedures. This study found that the reaction extent could be enhanced with the increase in both water content and the concentration of the catalyst. If the molar ratio of water versus ethoxyl groups is higher than 0.8, gelation can occur frequently. If water content in the system is not sufficient, it was also observed that the viscosity of the polymer prepared via stepwise monomer feeding could become markedly higher than the viscosity of the polymer prepared via monomer feeding with one

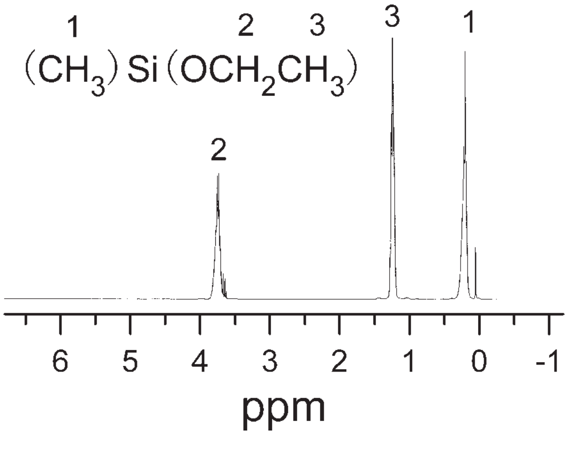


Figure 2 ^{1}H NMR spectrum of hyperbranched polyethoxysiloxane.

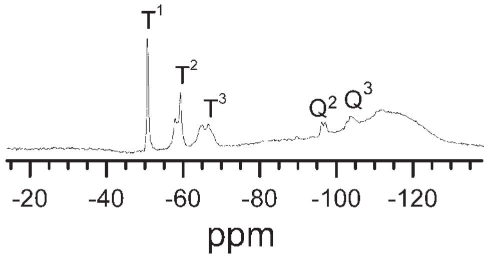


Figure 3 ^{29}Si NMR spectrum of hyperbranched polyethoxysiloxane.

pot. To get hyperbranched polyethoxysiloxane in which no water and silanol groups exist, it is necessary to add a small portion of water and use excessive amount of catalyst (HCl) following a stepwise monomer feeding procedure. Only in this way, the effort for removing both water and silanol groups from the system can be fulfilled. In addition, when the polycondensation reaction is completed, sodium carbonate must be added for removing resident hydrochloric acid, and distillation should also be performed to diminish the ethanol component produced during the reaction. The final product, a transparent and colorless viscous liquid, can be dissolved in various mixture organic solutions at any ratio including tetrahydrofuran, toluene, chloroform, hexane, ethanol, and *N*,*N*-dimethylformamide.

Characterization

Figure 1 shows FTIR spectrum of polyethoxysiloxane synthesized. According to the reference,[17] these IR bands can be assigned as follows: 2974 cm^{-1} (—CH_3, υ_{as}), 2885 cm^{-1} (—CH_2CH_3, υ_s), 1390 cm^{-1} (—CH_3, δ_s), 1269 cm^{-1} (Si—CH_3, δ_s), 1076 cm^{-1} (Si—O—Si), 769 cm^{-1} (Si—CH_3, υ_s). As there are no IR absorptions occurring between 3000 and 3500 cm^{-1}, it indicates that there are no silanol groups in the polymer.

The ^{1}H NMR spectrum of polyethoxysiloxane (Fig. 2) exhibits three chemical shifts corresponding to methyl protons (0.16 ppm, 37%) attached to a silicon atom, methyl (1.06 ppm, 38%), and methylene protons (3.76 ppm, 25%) in an ethoxyl segment attaching to a silicon atom. The integral area for each chemical shift indicates that the ratio of methyl versus ethoxyl groups in hyperbranched polymer is about 1.0.

^{29}Si NMR spectrum of polyethoxysiloxane is shown in Figure 3. The assignments of the chemical shifts of species formed in the reaction between TEOS and MTES are based on Refs. 18,19 and are listed in Table I. As can be seen from Figure 3, there are five main chemical shifts, which are labeled as T^1 (−51 ppm), T^2 (−59 ppm), T^3 (−66 ppm), Q^2 (−96 ppm), and Q^3 (−103 ppm). Among them, T^1, T^2, and T^3 represent silicon atoms containing 1, 2, and 3 —Si—O—Si— bonds formed via polycondensation of MTES, and Q^2 and Q^3 represent silicon atoms containing 2 and 3 —Si—O—Si— bonds formed via polycondensation of TEOS.[20] At the same time, T^1 can actually represent a terminal structure, and T^2 and Q^2 can represent a linear structure, and T^3 and Q^3 can represent a dendritic structure, respectively. Therefore, the integration of the peak for each chemical shift can lead to further calculation of the DB for hyperbranched polymer, using eq. (1).[21,22] The actual DB value calculated via eq. (1) is 0.67.

$$\mathrm{DB} = \frac{2\mathrm{T}^3 + \mathrm{Q}^3}{2\mathrm{T}^3 + \mathrm{T}^2 + \mathrm{Q}^3 + \frac{2}{3}\mathrm{Q}^3} \qquad (1)$$

The detailed hyperbranched structure based on the description above is shown in Scheme 3. It is also found from Figure 3 that there exist some splits of chemical shift for T^2, T^3, and Q^2, and these may result from the molecular internal cyclization reaction and the interference of adjacent silicon atoms.[19,20] Besides, there are no chemical shifts for silanol groups occurring in Figure 3 indicating that the process of condensation in the system could be completed.

GPC elution curve for hyperbranched polymer is shown in Figure 4. The weight average molecular weight is 6900 g/mol, with a polydispersity index of 2.67. It should be pointed out that there are two peaks

TABLE I
^{29}Si NMR Chemical Shift Assignment for Species in Polymer Synthesized

Species	δ (observed)	δ (Ref. 18)	Species	δ (observed)	δ (Ref. 19)
$SiOSi(OEt)_3$	–	−89.0	$MeSi(OEt)_3$	–	−42.6
. . . $SiOSi(OEt)_2(OH)$	–	−87.4	$MeSi(OEt)_2(OH)$	–	−41.1
. . . $SiOSi(OEt)(OH)_2$	–	−83.8	$MeSi(OEt)(OH)_2$	–	−39.8
. . . $SiOSi\ (OH)_3$	–	−81.8	$MeSi\ (OH)_3$	–	−38.5
. . . $SiO)_2Si(OEt)_2$	−96	−96.4, −95.2	. . . $SiOSiMe(OEt)_2$	−51	−50.5
. . . $SiO)_2Si(OEt)(OH)$	–	−93.5, −92.9	. . . $SiOSiMe(OEt)(OH)$	–	−49.0
. . . $SiO)_2Si(OH)_2$	–	−91.3, 90.6	. . . $SiOSiMe(OH)_2$	–	−47.7
. . . $SiO)_3Si(OEt)$	−103	−103 to −104	. . . $SiO)_2SiMe(OEt)$	−59	−58.6
. . . $SiO)_3Si(OH)$	–	−100.5 to −101	. . . $SiO)_2SiMe(OH)$	–	−56.8 to −57.0
. . . $SiO)_4$	–	−110	. . . $SiO)_3SiMe$	−66	−65.5

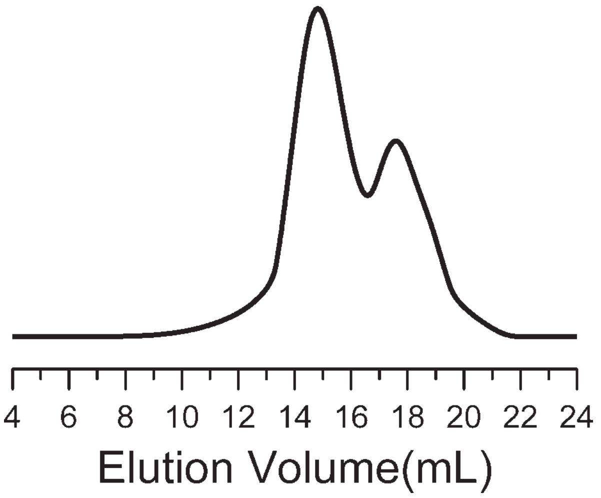


Figure 4 The GPC curve of hyperbranched polysiloxysiloxane.

in Figure 4, which may refer to the existence of some cyclic species produced from intramolecular reaction.

Preparation of antifouling coating based on hyperbranched polyethoxysiloxane

Using the properties of low surface energy, chemical stability, and excellent flow and permeability of hyperbranched polyethoxylsiloxane, a coating with excellent antifouling function for tile is prepared. The recipe of the coating is listed in Table II.

Ceramic products, such as polished tiles, are scratch resistant and also important for home decoration. However, there are still some deficiencies in ceramic products such as microcracks and pores on the surface of ceramic substrates. These defects may cause serious problems such as pollutants penetrating into the substrate via the capillarity effect.[23,24] Currently, silicon oil- and paraffin-based coatings are used to protect tiles. However, the interactions between coatings and substrates are so weak that they often easily become separated from the tiles and lose their function.[25] Based on these considerations, hyperbranched polyethoxysiloxane is designed and utilized as a binding component to develop an antifouling coating for tiles.

TABLE II
Recipe of the Coating Based on Hyperbranched Polyethoxysiloxane

Component	Composition (wt %)
HBPESS	45
Petroleum ether	32.4
Colorless kerosene	22.4
Dibutyltin dilaurate	0.2

Apart from binding component, other additives have an important effect on the coating. For example, solvents must be colorless, innocuous, low viscosity, hydrophobic, and have a high wetting property to substrates. Although only a small fraction of curing catalyst is needed, it is also crucial for the coating. This experiment indicates that DBTDL is a good catalyst for curing. The system with DBTDL as catalyst not only has a high curing speed, but also possesses excellent storage stability if water can be isolated completely from the system.[26]

To better understand the mechanism of antifouling related to the coating's composition, the surface state of the tile with coating application is tentatively divided into five grades according to its antifouling function, where grade 0 represents there is no any antifouling effect, while grade 4 indicates that both hydrophilic and hydrophobic pollutants cannot contaminate the substrate.[25] Besides these two extreme situations, grade 1, grade 2, and grade 3 are also marked according to the extent of contamination on the surface of the tile. Figure 5 shows the different antifouling effects on the substrate treated with the coatings with different solid content (SC). The SC for coatings can be calculated according to eq. (2).

$$SC = \frac{w_c}{w_i} \times 100\% \tag{2}$$

where w_i is the original weight of coating, and w_c is the weight of the completely dried coating.

From Figure 5, it can be seen that the coating has excellent fouling-prevention ability if the SC is over 15%. However, if the SC is less than 15%, the antifouling effect of the coating declines sharply. The results may indicate that less polymer binder can prohibit coating from forming a perfect protective membrane, and consequently result in the reduction of its antifouling function. On the other hand, if the SC is over 15%, the coating with low surface energy can feasibly form a nice membrane, and can quickly penetrate into defects and crosslink on the surface of the tile. As

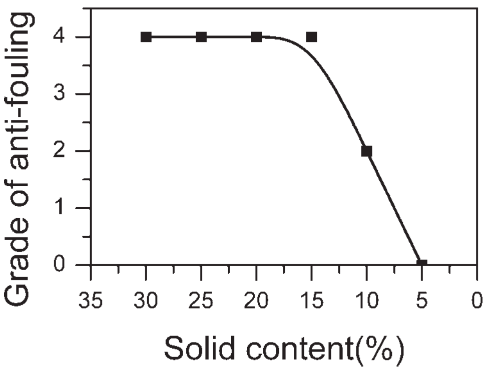


Figure 5 Antifouling effect of coating versus polymer's SC.

TABLE III
Surface State of Ceramic Substrates Before and After Applying Coating

	Before coating	After coating
Silicon element content (%)	75.2	76.7
Luster (degree)	58	63
Water uptake value (%)	0.177	0.011
Contact angle (degree)	60	93

shown in Table III, the excellent protective result of the coating can also be demonstrated by the measurements of contact angle on the surface of tile.

From Table III, it is very clear that after applying the coating, the contact angle increases markedly, and the luster of the tile also improves obviously. This indicates that it is indeed an excellent antifouling coating for tile.

Figure 6 shows the surface image of the tile with and without coating, using SEM. The fuscous part is the substrate of the tile, and the light-colored part is the defects. Obviously, there are a lot of defects on the surface as shown in Figure 6(a), where the minimum size of a crack is about several microns, and the maximum size is more than 100 μm. After applying the coating, the size of the cracks reduces, and the surface

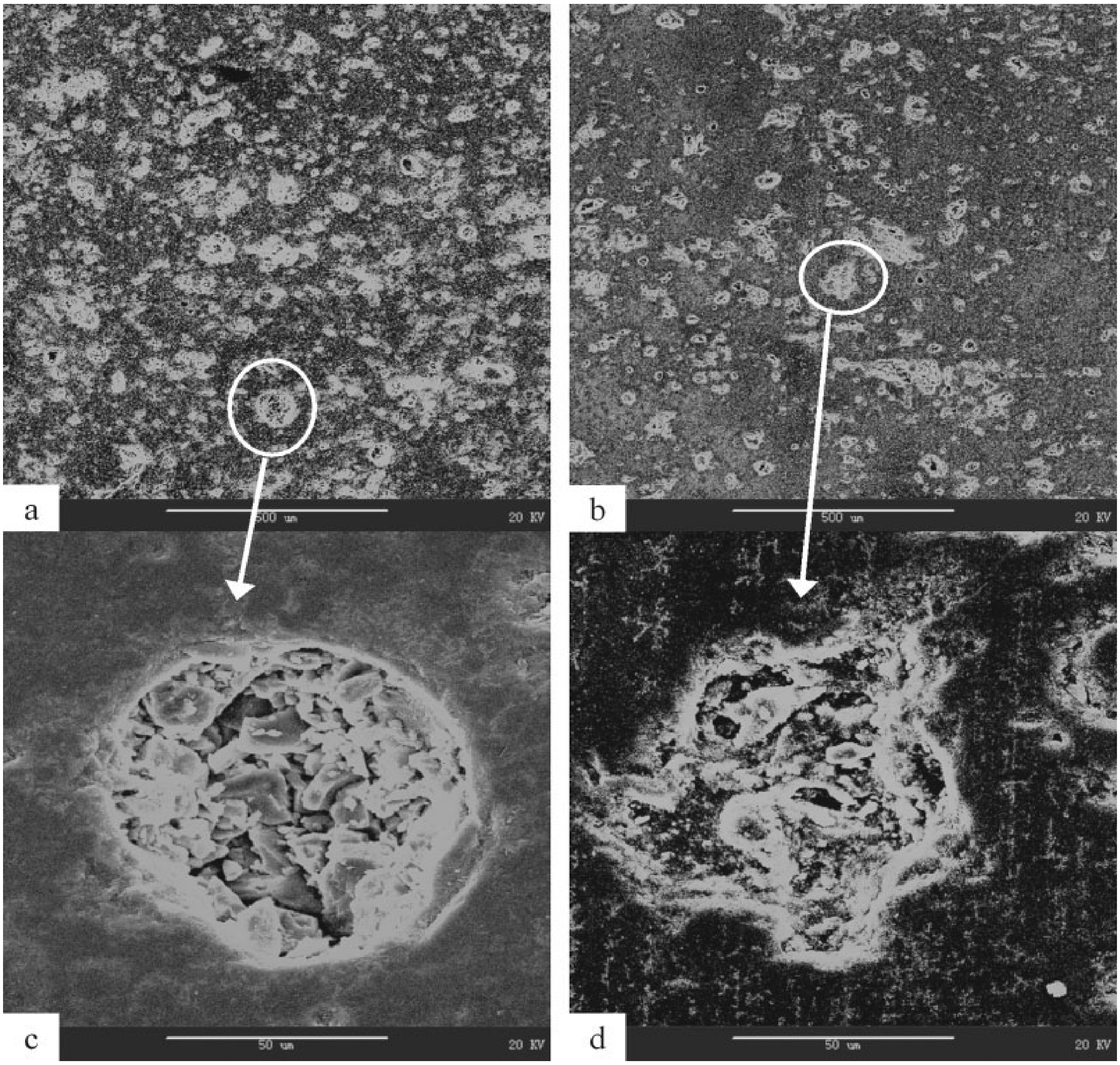


Figure 6 Surface micrograph of a tile with and without applying coating: (a) substrate before applying coating, (b) substrate after applying coating, (c) a pore on the surface of tile before applying coating, (d) a pore on the surface of tile after applying coating.

state is obviously improved as can be seen from Figure 6(b). It can also be observed from Figure 6(c) that there are a lot of scrapes in the pore, which may be produced during the polishing process. After coating, as shown in Figure 6(d), polyethoxysiloxane penetrated into the pore and crosslinked with the scrapes. Consequently, it fastened the scrapes and filled the pores on the surface of tiles.

CONCLUSIONS

Hyperbranched polyethoxylsiloxane can be synthesized via polycondensation of TEOS and MTES under the acidic condition. The characterizations by FTIR, ^{1}H NMR, ^{29}Si NMR confirmed that polyethoxylsiloxane synthesized is indeed a herpybranched polymer with a DB of 0.67. GPC data show that the weight average molecular weight of the polymer is 6900 g/mol, with a polydispersity index of 2.67. By using the synthesized polymer as binder, a novel antifouling coating was developed. From the contact angle measurements and SEM inspection, the antifouling mechanism of the coating is studied. This research revealed that over 15% of SC, the coating could feasibly form a perfect membrane via penetrating and crosslinking on the surface of tiles, and possessed an excellent antifouling effect.

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