Silica-Embedded Polyurea Microspheres with Rough Surface for Matte Leather Finishing

by

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Abstract

A type of polyurea microspheres with rough surfaces and different sizes (1-12 μm), which was used for waterborne polyurethane matte leather coating, were prepared by precipitation polymerization in H_2O/acetonitrile system, using isophorone diisocyanate as polymerized monomer, 2,4-diaminobenzenesulfonic acid sodium salt as hydrophilic monomer and nano-SiO_2 as surface roughener. The effect of the loading of isophorone diisocyanate and 2,4-diaminobenzenesulfonic acid sodium salt, the volume ratio of H_2O/acetonitrile and the addition stage of nano-SiO_2 on the particle size and surface roughness were investigated so as to achieve the excellent matte effect of the coating. The results indicated that the adding of hydrophilic monomer can reduce the particle size of microspheres and improve its re-dispersibility in water, while the increase of the proportion of acetonitrile in the mixed solvent and the loading of polymerized monomer can enlarge the size of the polyurea microspheres. As surface roughener, with the increase of nano-SiO_2 loading, the surface roughness and the particle size of microspheres increase. When nano-SiO_2 is added at the stage of the reaction system getting turbid, the maximum surface roughness of polyurea microspheres can be achieved. Polyurea microspheres with particle size (1-2 μm) and high surface roughness have better matting effect, and the gloss of the prepared waterborne polyurethane coating can be adjusted to less than 1.6° (60°-incident Angle).

Introduction

As a thin film covering the surface of the substrate, the primary functions of the coating include covering up the surface defects, protection for substrate, improving its waterproofness and so on. In addition, coating can also endow the substrate with beautiful color and various aesthetic effects.[1] With the development of aesthetic, the requirements for the color and gloss of coatings are continuously changing, the matte coatings become more and more popular[2-4] and widely used in automotive, furniture, costume and other fields.[5] According to the optical theory, a rough surface is a key issue to achieve matte effect during the coating formation. Higher surface roughness always leads to a lower surface gloss.[6] Currently, the most economical way to obtain matte coatings is by adding a variety of matte fillers into the coatings, and the matte fillers are often composed of inorganic or organic materials, such as nano-fumed SiO_2 and wax. However, the inorganic powders often cause a series of drawbacks, such as poor compatibility, worse hand feeling and low adhesion with substrate (the coating will get white by stretching).[7-9] In order to solve these problems, the research for organic matte fillers which have excellent matte effect and good affinity with waterborne polyurethane (WPU) emulsion and substrate has become a hotspot.

As a widely used organic polymer material, polyurea has excellent abrasion performance, weather durability and thermal shock resistance.[10] Furthermore, WPU has been widely used in leather/synthetic leather finishing, textile laminating, automobiles and wood coatings for its environmental friendliness and excellent comprehensive performance.[5] On account of the similarity of structure between polyurea and WPU, they should have good affinity to each other. Given a controllable size and micro-roughness surface, the microspheres themselves would have light scattering characteristics.[11,12] Meanwhile, adding different-sized microspheres into the coating can form a rough coating surface and produce matte effect.[13] The synergy of the two features is believed to give the coating superimposed matte effect.

Traditional methods for preparation of polyurea microspheres include suspension polymerization,[14] emulsion polymerization[15] and precipitation polymerization.[16] Nevertheless, the preparation of microspheres with controllable particle size and rough surfaces is still a challenge for a long time through a multiple phase system.[12] Although many works have been done to prepare microspheres with various special structures,[17] such as Walnut-like particles,[11] golf ball-like polymer particles[12] and porous microspheres[18] etc.; few studies were focused on how to control the gloss of coatings by controlling the size and morphology of particles. Meanwhile, there are few reports about the hydrophilicity of polyurea microspheres.

In this study, a series of polyurea microspheres with different sizes and surface roughness, were prepared by adjusting the loadings of 2,4-Diaminobenzenesulfonic acid sodium salt (MPDSA-Na), isophorone diisocyanate (IPDI) and surface roughener (nano-SiO_2

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powder), the volume ratio of acetonitrile (AN) and H_2O, and the addition stage of nano-SiO_2. Meanwhile, the influence of particle size and surface of microspheres on the matte effect of WPU coating were investigated.

Experimental

Materials

IPDI was acquired from Dymatic Post Polymer Material Co. (Lishui, China). MPDSA-Na and nano-SiO_2 were obtained from Aladdin. The AN solvent was supplied by Kelong Chemical Engineering Co. Ltd (Chengdu, China). WPU(35% solid content) was obtained from Lanxess Co. All chemicals were used as received unless stated otherwise.

Preparation of polyurea microspheres with different surface roughness[19]

Preparation of polyurea microspheres with smooth surface: Figure 1 shows the reaction steps of IPDI. H_2O/AN mixture (100g, 1/4, 3/7, 2/3) was first charged into the reaction bottle, followed by addition of IPDI (1 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt%), and MPDSA-Na (6 wt%, 10 wt%, 14 wt% and 18 wt% of the IPDI). The bottle was sealed off, hand-shaken to make the mixture homogeneous, and left standing still (without any oscillation or stirring) in a water bath at 50°C for 5 hours.

Preparation of polyurea microspheres with rough surface: Nano-SiO_2 was used as surface roughener. IPDI, MPDSA-Na and nano-SiO_2 (0 wt%, 60 wt%, 80 wt% and 100 wt% of the IPDI) were dissolved in H_2O/AN solution to form a homogenous solution. The bottle was sealed off, and the precipitation polymerization was carried out in a water bath for 3 h at 50°C under oscillation.

Samples were centrifuged for 5 min at 4000 rpm. Then the precipitate was filtered and washed with deionized water for 5 times so as to remove the unreacted hydrophilic monomer MPDSA-Na and other water-soluble impurities. Finally, the precipitate was dried for 6 h at 80°C and the microspheres were obtained.

Preparation of WPU matte coating[13]

The polyurea/WPU composite was prepared by adding 5 wt% polyurea microspheres (based on WPU emulsion), small amount of flowing agent (1.6 wt%) and thickening agent (1 wt%) into WPU. The mixture was stirred in a beaker at 500 rpm until the viscosity reached 1000 mPa.s, and then coated it on the synthetic leather and natural leather surface with a drying process at 120°C for 3–5 minutes.

Characterization

The element and structure of the polyurea microspheres were analyzed by X-ray photoelectron spectroscopy(XPS) and Fourier infrared spectrometer(FTIR). And the morphology of microspheres was observed by scanning electron microscope (SEM, JSM-7500F, Japan). Size (Dn) and size distribution (Dw/Dn) were calculated by counting about 200 microspheres on the SEM pictures.[20] Re-dispersibility was tested by adding the polyurea microspheres into deionized water to observe the sedimentation velocity of the microspheres.[21,22] Glossmeter (REFO 60, Germany) was used for measurement of surface gloss with a 60°-incident angle. Each sample was tested five times on different districts and its average data was reported.

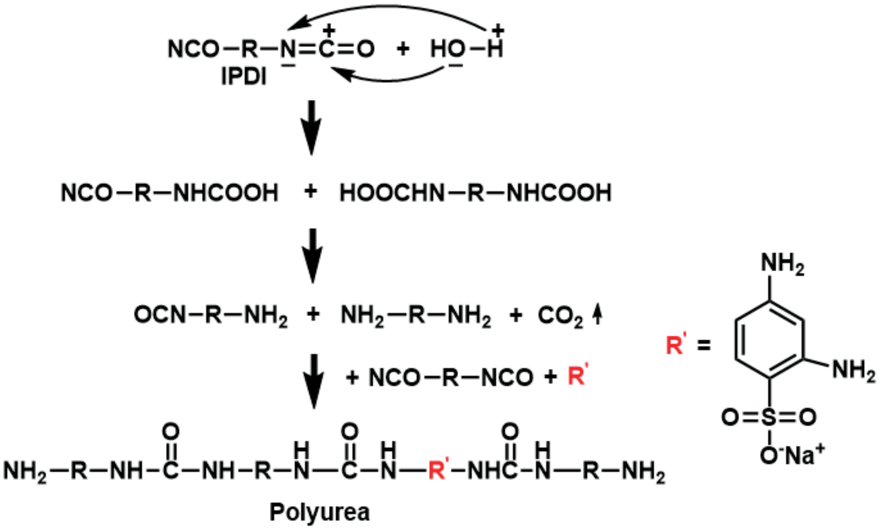

Figure 1. The reaction steps of IPDI

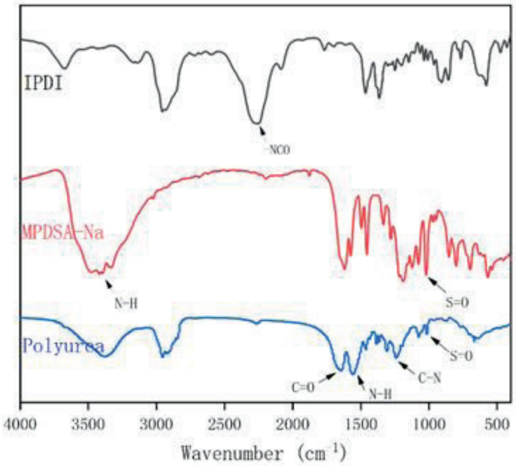

Figure 2. The FTIR spectra of polyurea microspheres

Results and discussion

Structural of polyurea microspheres

IPDI, MPDSA-Na and purified polyurea microspheres with smooth surface were analyzed by FTIR and XPS respectively. In FTRR of IPDI in Figure 2, the absorption peak at 2264 cm^{-1} confirmed the -NCO stretching vibration, after polymerization, this peak disappeared. In FTIR of hydrophilic monomer MPDSA-Na, the peak at 3419 cm^{-1}, 1190 cm^{-1} respond to the N-H stretching vibration and the S=O stretching vibration in the sulfonic acid group. Correspondingly, these peaks occurred in the FTIR of the polyurea microsphere at 3379 cm^{-1} (ascribed to the N-H stretching vibration in -NHCONH-) and 1190 cm^{-1} (assigned to the stretching vibration of S=O in sulfonic acid group) separately,[16] which indicate that the hydrophilic group was successfully grafted to the surface of the polyurea microspheres.

In Figure 3 of XPS analysis, the binding energy at 167.2eV referred to the characteristic peak of S2p, which was identified as the characteristic peak of S element in the sulfonic acid group.[23] Combined with FTIR and XPS analysis, it was shown that the MPDSA-Na had reacted with IPDI and the sulfonic acid group was introduced to the surface of polyurea microspheres.

Influence of MPDSA-Na loading on microsphere size and its re-dispersibility

As a matte filler for WPU coating, polyurea microspheres should have re-dispersibility in water. But the polyurea microspheres are hard to be re-dispersible in WPU due to its-hydrophobicity.[24] To solve this problem, hydrophilic monomer MPDSA-Na is used to improve their hydrophilicity and re-dispersibility. Figure 4 shows the size and dispersion of the polyurea microspheres with 6 wt%, 10 wt%, 14 wt% and 18 wt% MPDSA-Na loadings (based on IPDI, respectively). As can be seen that polyurea microspheres with 6 wt%-10 wt% MPDSA-Na loadings show larger size and good dispersion, whilst with 18 wt% MPDSA-Na shows uneven size and poor dispersibility, for 18 wt% loading, some microspheres even appeared agglomerated. The results indicated that the high an amount of MPDSA-Na was not conducive to obtain polyurea microspheres with good dispersion. Table I lists the particle size variation of polyurea microspheres with the MPDSA-Na loading. When the loading increased from 6 wt% to 18 wt%, the particle size of polyurea microspheres decreased from 9.31 μm to 6.04 μm, showing a decreasing trend. The reason could be ascribed to the enhanced charge density, which prevents primitive particles from approaching and fusing with each other to form large-size microspheres.[13] The best loading is 14 wt% for that the microspheres have better hydrophilicity and not agglomerate like Figure 4d.

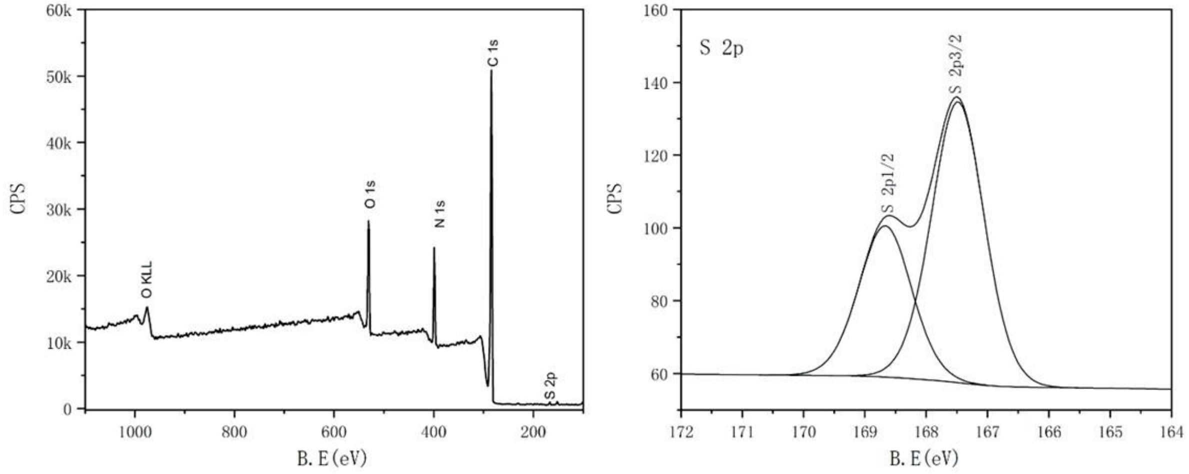

Figure 3. The XPS analysis of polyurea microspheres

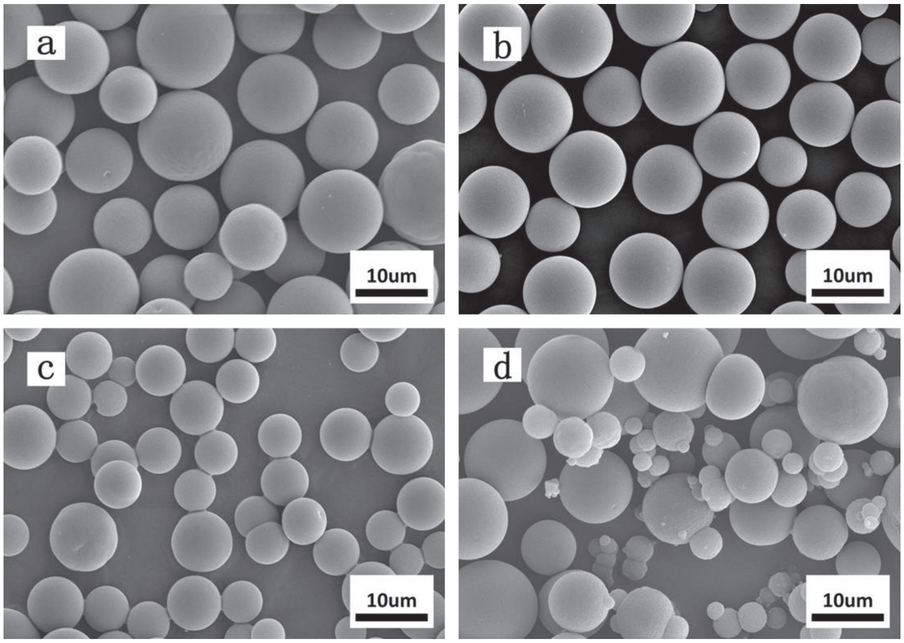

Figure 4. The effect of MPDSA-Na loading (wt%) on polyurea microsphere size: **(a)** 6; **(b)** 10; **(c)** 14;**(d)** 18.

Table I

D_n and D_n/D_w of polyurea microspheres at different MPDSA-Na loading

	MPDSA-Na loading (wt%)	D_n/μm	D_w/μm	D_n/ D_w
a	6	9.31	11.59	1.24
b	10	8.66	9.92	1.15
c	14	6.83	7.81	1.14
d	18	6.04	12.06	1.99

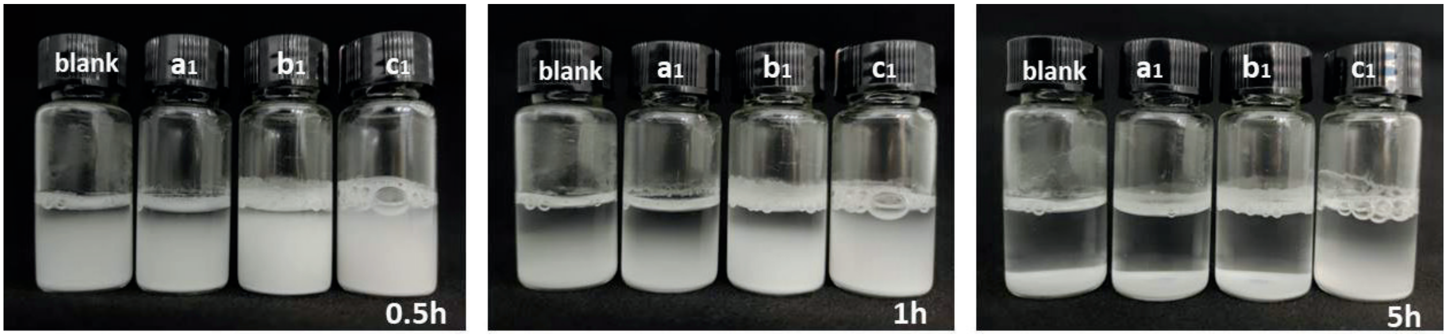

Figure 5. The dispersion stability of polyurea microspheres understanding for different periods

Table II

D_n and D_n/D_w of polyurea microspheres at different H_2O/AN

	H_2O/AN	D_n/μm	D_w/μm	D_n/ D_w
a	2/3	5.38	6.49	1.21
b	3/7	6.83	7.81	1.14
c	1/4	8.82	11.53	1.31

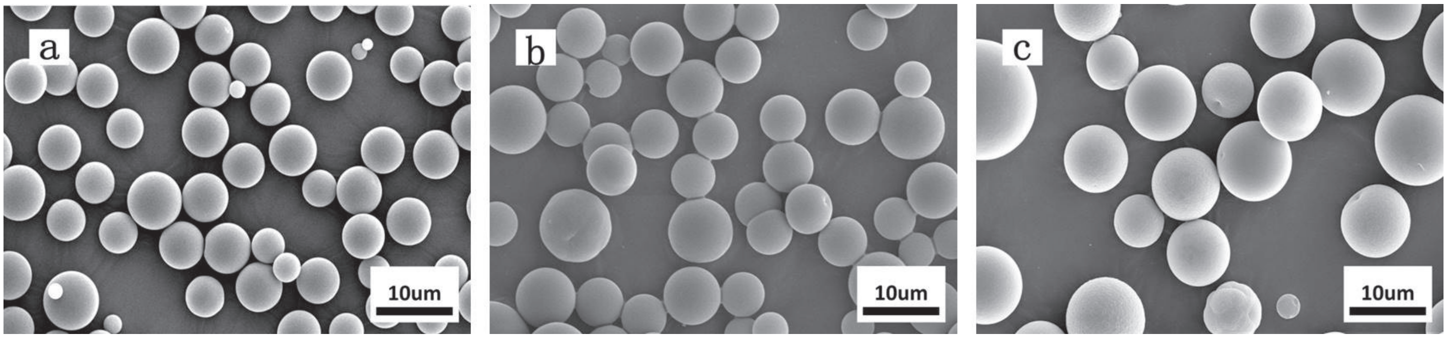

Figure 6. The effect of H_2O/AN on polyurea microsphere size: **(a)** 2/3; **(b)** 3/7; **(c)** 1/4

The polyurea microspheres without hydrophilic groups (blank) and the polyurea microspheres a, b and c mentioned in Figure 2 were added to the deionized water to form 2 wt% dispersion solution and named blank, a_1, b_1 and c_1 respectively (Figure 5). The polyurea microsphere dispersion was left standing at room temperature and photographed after 0.5 h, 1 h and 5 h to observe their dispersion state. It can be seen that after 0.5 h of standing, stratification began to occur in a_1, b_1 and blank. After standing-for 1 h, c_1 also began to stratify. After standing for 5 h, the microspheres in a_1, b_1 and blank were completely precipitated, while those in c_1 were not completely precipitated. The results show that increasing the loading of hydrophilic monomer can improve the dispersion stability of the microspheres in water.

Influence of H_2O/AN volume ratio on microsphere size

Volume ratio of H_2O/AN can change the polarity of the mixed solvent. Higher proportion of AN in the solvent will increase the solubility of IPDI and its oligomer. In addition, water in the solvent also participates in the reaction, its amount imposes an obvious effect on the particle nucleation.[19] Therefore, solvent volume ratio has an important effect on the size of microspheres. Figure 6 shows the size variation of polyurea microspheres in different H_2O/AN volume ratio (2/3, 3/7, 1/4, respectively). The corresponding size of the microspheres obviously enlarged from 5.38 μm to 8.82 μm with AN content in the mixed solvent increased from 60% to 80% (Table II). The increasing trend is attributed to the increased solubility of the oligomers in the solvent. At the same time, narrower size distribution was obtained for the runs with H_2O/AN volume ratio at 3/7, while the uniformity of microspheres deteriorated with enlarged size distribution (H_2O/AN volume ratio at 2/3 and 1/4). It can be argued that polymerization in the binary solvent with a low AN amount creates a huge number of primitive particles, leading to their partial or limited aggregation during the process; whereas polymerization in the solvent with a higher AN content postpones particle aggregation, resulting in an extended and continuous nucleation. Both of the two circumstances will cause a broadened size distribution for the microspheres.

Influence of IPDI loading on microsphere size

On account of that high IPDI loading in the binary solvent can create a huge number of primitive particles, the amount of it has an important effect on the size of the microspheres in precipitation polymerization.[22,25]

Figure 7 shows the size of polyurea microspheres prepared with different IPDI loading (1 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt%, respectively). When the IPDI loading was increased from 1 wt% to 10 wt%, the microspheres did not agglomerate and could form independent microspheres with good dispersion. As shown in Table III, the particle size of microspheres enlarged from 2.55 μm to 11.48 μm with the increase of the IPDI amount from 1 wt% to 10 wt%. Generally, the increase of the IPDI loading can enhance the concentration of primitive particles, and the collision probability among primitive particles will increase. Therefore, there are more small particles fused to form large particles. Besides, the D_n/D_w of microspheres are found to be related to the IPDI loading, when the IPDI loading is 1 wt% and 4 wt%, the D_n/D_w of microspheres are 1.01 and 1.02 and are close to highly uniform size.[25] When

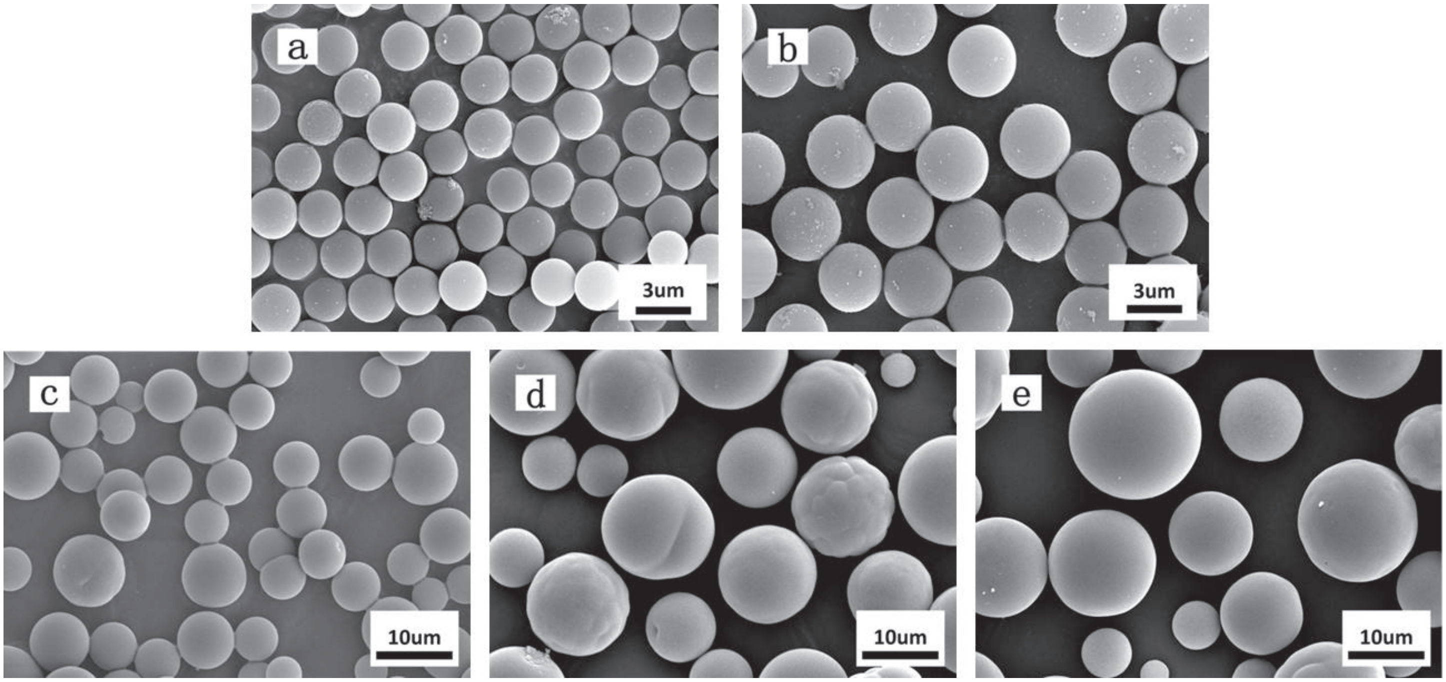

Figure 7. The effect of IPDI loading (wt%) on polyurea microsphere size: **(a)** 1; **(b)** 4; **(c)** 6; **(d)** 8; **(e)** 10

Table III

Dn and Dn/Dw of polyurea microspheres at different IPDI loading

	IPDI loading (wt%)	D_n/μm	D_w/μm	D_n/ D_w
a	1	2.55	2.57	1.01
b	4	3.56	3.62	1.02
c	6	6.83	7.81	1.14
d	8	10.70	12.94	1.21
e	10	11.48	14.56	1.28

the IPDI loading is above 4 wt%, the size microspheres exhibited polydispersity. This is highly possible because there are still many primitive particles in the binary solvent when large-size microspheres formed in the system, which leads to the increase of D_n/D_w.

In terms of matte coating, it is noted that the larger the size of the microsphere, the worse the matte effect appeared. When the microspheres are large enough to form a smooth surface for themselves, they cannot scatter the incident light, so good matting effect cannot be achieved. That is, even if the size and dispersity of the polyurea microspheres are well controlled, the microspheres with smooth surface could not give the coating ideal matting effect.

Effect of nano-SiO_2 loading on surface roughness of polyurea microspheres

In order to increase the light scattering characteristics of the surface, nano-SiO_2 was used as surface roughener to create the roughness on the surface of microspheres. Figure 8 shows the surface roughness of polyurea microspheres with different nano-SiO_2 loadings (0 wt%, 60 wt%, 80 wt% and 100 wt% of the IPDI, respectively). As can be seen from Figure 8, the polyurea microspheres with different nano-SiO_2 loadings did not agglomerate but formed independent microspheres with good dispersity. Most importantly, all polyurea microspheres exhibited a rough surface with the addition of nano-SiO_2. Compared with the control sample (3.56μm) without nano-SiO_2 in Figure 8 and Table IV, the particle size of other microspheres enlarged from 5.93 μm to 9.26 μm with the increase of nano-SiO_2 loading from

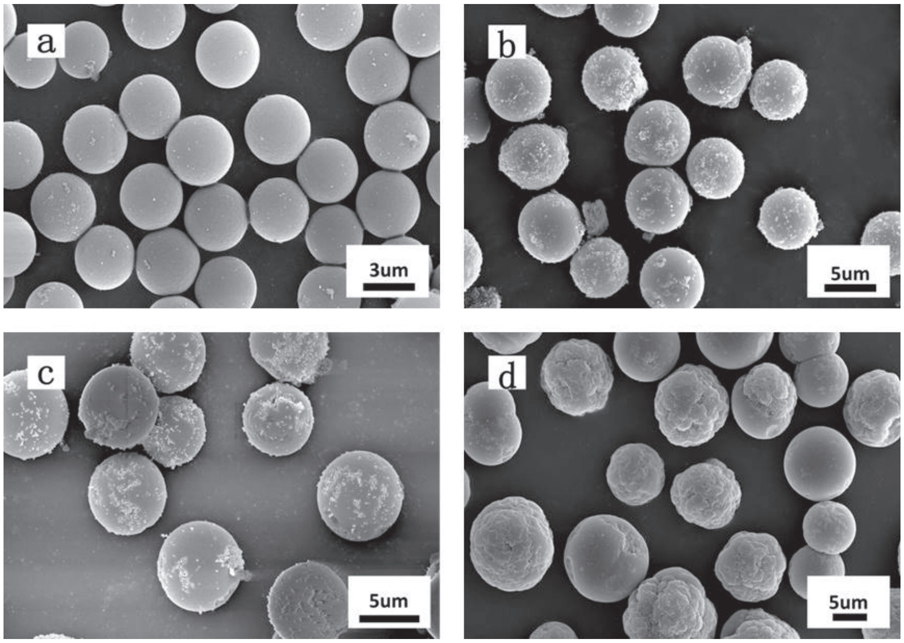

Figure 8. The effect of nano-SiO_2 loading (wt %) on polyurea microsphere size and morphology: **(a)** 0; **(b)** 60; **(c)** 80; **(d)** 100.

Table IV

D_n and D_n/D_w of polyurea microspheres at different nano-SiO_2 loading

	SiO_2 loading (wt %)	D_n/μm	D_w/μm	D_n/ D_w
a	0	3.56	3.62	1.02
b	60	5.93	6.07	1.02
c	80	6.58	6.77	1.03
d	100	9.26	9.84	1.06

60 wt% to 100 wt%, the reason could be that nano-SiO_2 enters the microsphere core and increases the microsphere size.

Influence of nano-SiO_2 addition stage on surface roughness of polyurea microspheres

Figure 8 shows that increasing the amount of nano-SiO_2 could only improve the surface roughness of polyurea microspheres to a certain extent. Further analysis theorized that a large amount of nano-SiO_2 could be wrapped in the interior of polyurea microspheres, leading to the surface of the polyurea microspheres not being so rough. So, the addition stage of nano-SiO_2 was changed to confirm the above theory. Figure 9 shows the surface morphologies of polyurea microspheres prepared by adding nano-SiO_2 at different stages (at the beginning of the reaction, at the stage of the reaction system getting turbid, and half an hour after the reaction system getting turbid). As can be seen from Figure 9, the relative surface roughness of polyurea microspheres is greater for nano-SiO_2 added at the stage of the reaction system getting turbid than for others. When the nano-SiO_2 was added at the beginning of the reaction, a large loading of nano-SiO_2 was wrapped inside the polyurea microspheres during the reaction process, resulting in low surface roughness of the microspheres. When the nano-SiO_2 was added half an hour after the reaction system began increasing in turbidity, plenty of nano-SiO_2 particles were adsorbed on the surface of the microspheres and the space between them thus, no rough surfaces were formed. When the nano-SiO_2 was added at the stage of the reaction system becoming turbid, a large number of particles grew to be insoluble in mixed solvents and began to precipitate, in this case, the added nano-SiO_2 was embedded on the surface of polyurea microspheres during the precipitation process, thus embedded nano-SiO_2 particles give the microspheres the maximum surface roughness (Figure 9b).

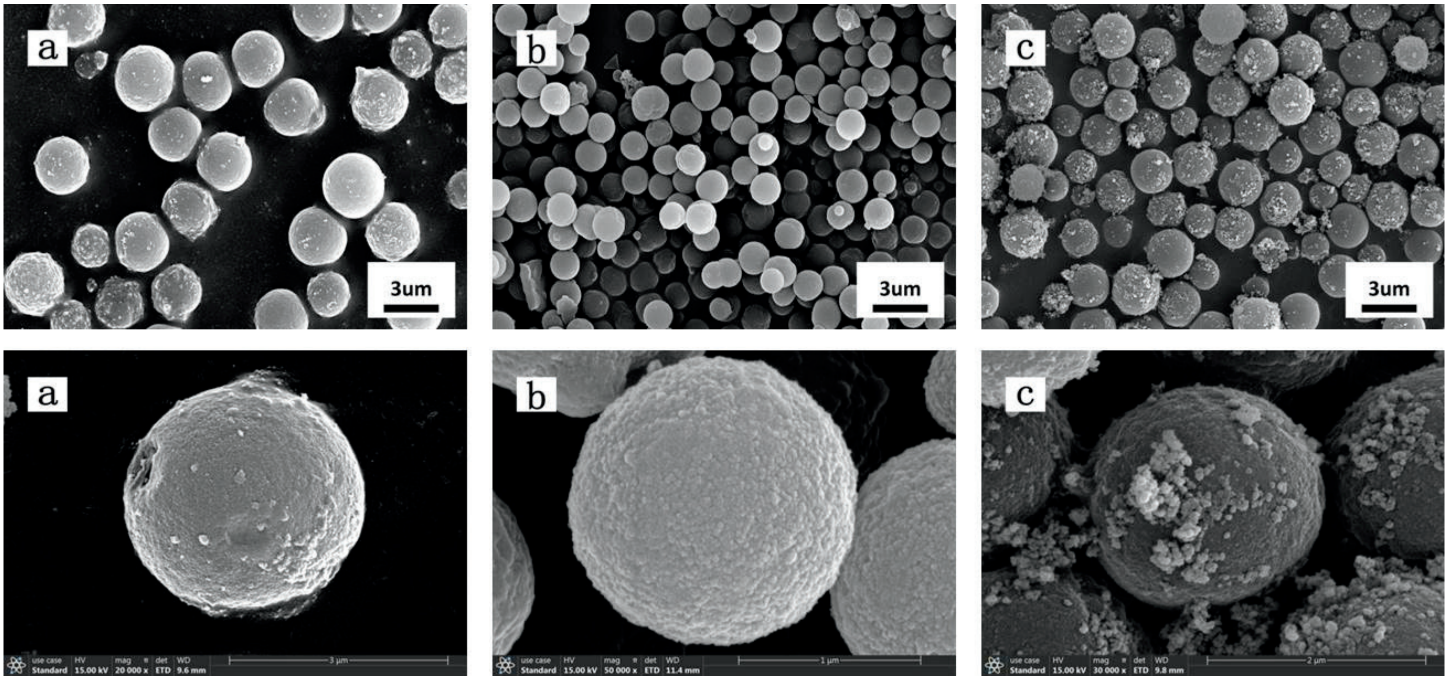

Figure 9. The effect of adding nano-SiO_2 at different stages on polyurea microsphere size and morphology: **(a)** at the beginning of the reaction; **(b)** at the stage of the reaction getting turbid; **(c)** half an hour after the reaction getting turbid

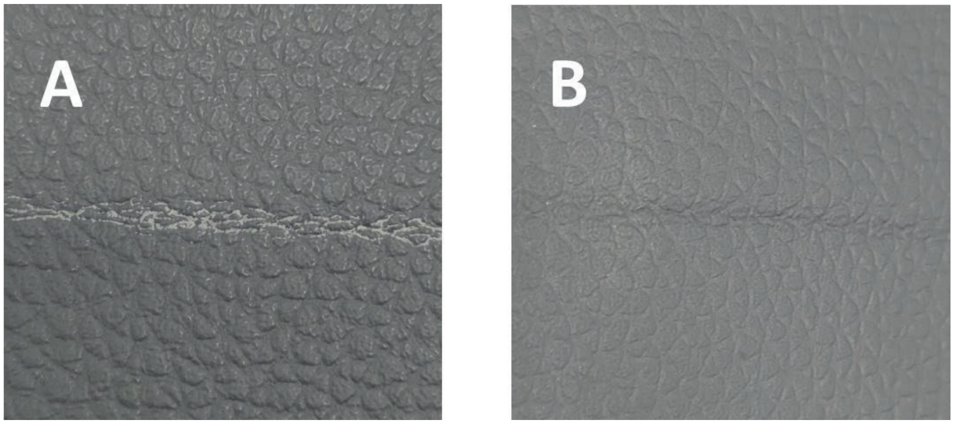

Figure 10. The digital photos of surface coated with: **(A)** SiO_2-embedded matteing powder; **(B)** polyurea microspheres

Table V

The polyurea microspheres with different sizes and size distribution

sample	D_n/μm	D_n/ D_w	SEM images
a	11.48	1.28	Fig. 7 e
b	9.31	1.24	Fig. 4 a
c	6.83	1.14	Fig. 4 c
d	9.26	1.06	Fig. 8 d
e	2.90	1.04	Fig. 9 a
f	1.49	1.07	Fig. 9 b

Influence of different polyurea microspheres on the gloss of WPU coating

Just as mentioned above, the addition of inorganic matting powder usually results in the decrease of adhesion of the coating, and the coating often gets white after stretching and hot pressing. Figure 10 shows the comparison of coatings with added SiO_2 matte powder and polyurea microspheres. The sample shown in Figure 10-A (coated with SiO_2-embedded matte powder) obviously becomes white after folding, while the one shown in Figure 10-B (coated with polyurea microspheres) does not become white after stretching and folding, which reveals that the coating with polyurea microspheres has no negative effect on adhesion.

The influence of different polyurea microspheres on the gloss of WPU coating was studied, and the particle size and surface morphology of these microspheres were listed in Table V.

Figure 11 shows the gloss of the corresponding synthetic leather coating with different microspheres listed in Table V. It can be seen that the gloss of blank coating without adding polyurea microspheres is 5.73° and the gloss of other coatings decreased to 1.27°-2.9° after adding 5 wt% polyurea microspheres in WPU, indicating that all microspheres have an ability to reduce the coating's gloss. When the particle size of the polyurea microspheres with smooth surface decreased from 11.48 μm to 2.55 μm, the corresponding gloss of the coating decreased from 2.9° to 2.03°, indicating that small particle size contributes better matting effect. Similarly, when the particle size of the polyurea microspheres with rough surface decreased from 9.26 μm to 1.49 μm, the gloss of the corresponding coating decreased from 2.4° to 1.57°. This indicates that small particle size and rough surface impart the coating higher matting effect. Comparing with the microspheres (b) and (d) with similar particle size (9.31 μm and 9.26 μm) but different surface roughness the gloss of corresponded coating are 2.4° (b_1) and 2.77° (d_1), also indicating the microspheres with rough surface show higher matting characteristics. The microspheres (d) keep good consistency with our experimental expectation.

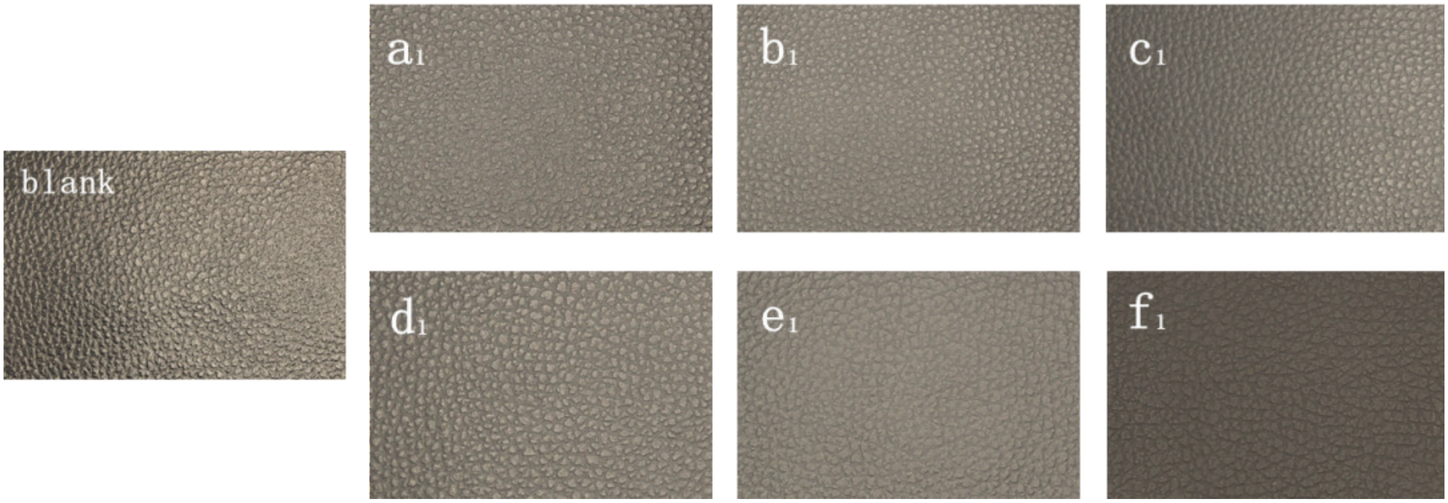

Figure 11. The digital photos of coating surface with different types of polyurea microspheres (listed in table V)

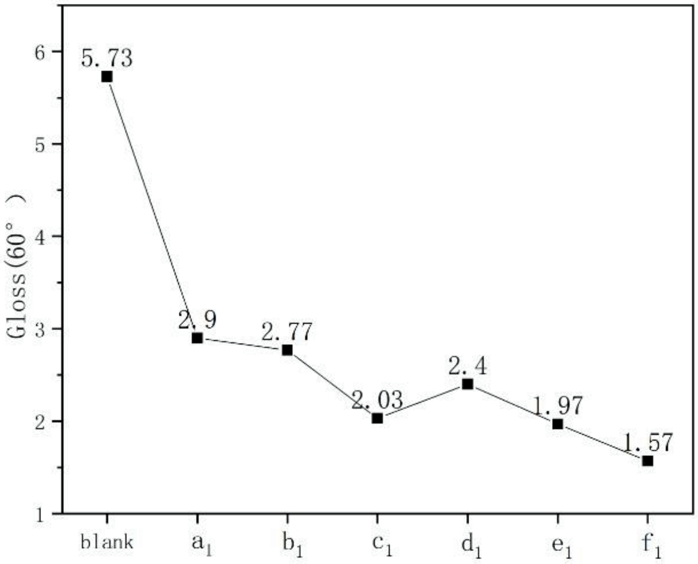

Figure 12. Glossiness of the corresponding coating in Figure 11

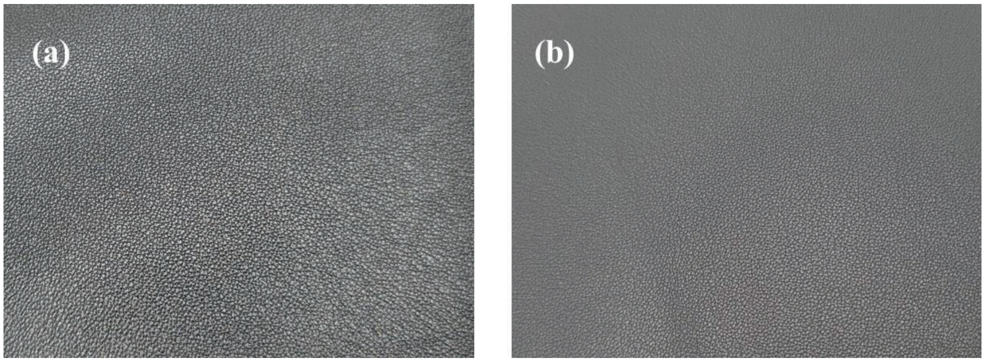

Figure 13. The digital photos of natural leather with different coating surface: **(a)** blank coating; **(b)** coating containing rough surfaced polyurea microspheres

Figure 13 shows the gloss of the natural leather coating with and without rough surfaced polyurea microspheres. The gloss of Figure 13 (a) is 3.90, and the gloss of Figure 13 (b) is 1.53. The results indicate that the coating containing rough surfaced polyurea microspheres also has excellent matting effect on the natural leather.

Conclusion

Polyurea microspheres with different sizes and surface roughness were prepared by precipitation polymerization in H_2O/AN system. And the effects of the loading of MPDSA-Na and IPDI, the volume ratio of H_2O/AN and the addition stage of nano-SiO_2 on the size and surface roughness of microspheres were investigated in detail. Furthermore, the effects of different polyurea microspheres on the gloss of WPU coating were also investigated. The results show that the re-dispersibility of as-prepared microspheres in water can be ensured with 14 wt% MPDSA-Na. The size and size distribution of the microspheres can be controlled by the loading of IPDI, MPDSA-Na, nano-SiO_2 and the volume ratio of H_2O/AN, whilst the surface roughness of the microspheres strongly relies on the addition stage of nano-SiO_2. Under the optimized condition of 1 wt% IPDI(based on solvent), 14 wt% MPDSA-Na (based on IPDI), 80 wt% nano-SiO_2 (based on IPDI), 3:7 H_2O/AN volume ratio and 50°C reaction temperature, the size of polyurea microspheres can be controlled in a range of 1.49 μm to 2.9 μm with monodispersity and higher rough surface. When 5 wt% microspheres are mixed with WPU for leather coating, no negative effect on adhesion is observed. Finally, the polyurea microspheres with particle size between 1-2μm and high surface roughness imparted the coating excellent matting effect, and the gloss of the resultant leather coating can be decreased from 5.73° to less than 1.6°.

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Authors' contributions

Liang Jia: Conceptualization, Methodology, Formal analysis, Writing - Original Draft, Jing Li: Data curation, Formal analysis, Li Wang: Validation, Investigation, Yi Chen: Visualization, Jun Xiang: Writing- Reviewing and Editing, Validation, Jun Yan: Validation, Haojun Fan: Writing - Review & Editing, Supervision.

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Availability of data and materials

All data generated or analyzed during this study are included in this article.

Declarations

Competing interests

The authors declare no competing interest.

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