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Improvement in properties of epoxy-based electrophoretic coating by silica/polyurethane nanocomposites

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Abstract Silica/polyurethane (SiO_2/PU) nanocomposites, prepared by in situ formation of silica from tetraethoxysilane (TEOS) in cationic polyurethane microreactor, are used to modify epoxy resin-based electrophoretic coating. The co-electrophoresis property of silica/PU nanocomposites with epoxy particles is verified by X-ray photoelectronic spectroscopy (XPS) analysis of the electrophoretically prepared membrane. The particle sizes and size distribution in the aqueous paint show a considerable reduction as demonstrated by dynamic light scattering. The surface morphology is investigated by scanning electron microscope. The properties of SiO_2/PU-modified electrophoretically prepared membrane have a significant improvement compared to those of unmodified and PU-modified membranes. It is noteworthy that both strength and toughness of the electrophoretically prepared membrane increase considerably due to incorporation of rigid silica encapsulated by tough PU.

Introduction

With increasing demand of environmental protection, water-based coatings are of growing interest due to their environment-friendly feature. A lot of efforts have been made on the improvement of their properties such as mechanical properties and corrosion resistance.

Polymer-based nanocomposites have received considerable attention recently because they are expected to combine the advantages of both organic polymers and inorganic nanoparticles and outstanding properties can be obtained with the addition of only a small amount of inorganic nanoparticles. It is well known that silica nanoparticles can effectively improve various properties of polymer matrices, such as strength, hardness, dimensional stability [1–7] etc. However, no much work concerns water-based coatings, in particular, electrophoretic coatings. Since no charges on the surface of silica nanoparticles, they could not be co-electrophoresed with ionic polymer, making their use in electrophoretic coatings difficult.

We recently reported a preparation of silica/polyurethane nanocomposites by a sol–gel process where silica nanoparticles are generated in situ in cationic PU capsules [8]. The availability of such silica/PU composite particles having positive charges on the surfaces gives us an opportunity to investigate the use of silica nanoparticles in electrophoretic coatings. Other assets which could be gained from the use of silica/PU nanocomposites are that the common problems encountered in ordinary polymer-based composites, such as agglomeration of silica primary particles and the incompatibility of inorganic silica with organic polymer matrix, could be effectively overcome.

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In the present work, we report a detailed study on silica/PU-forced epoxy-based electrophoretic coatings. The particle sizes and size distribution in the aqueous paint are investigated by dynamic light scattering. The co-electrophoresis of silica/PU composite particles and the epoxy particles are proved by X-ray photoelectronic spectroscopy (XPS) analysis of the electrophoretically prepared membrane. The surface morphology of the membranes is observed by scanning electron microscope (SEM) and discussed based on particle sizes and size distribution. The properties of the silica/PU-reinforced epoxy-based electrophoretically prepared membrane are evaluated and compared with those of unmodified and PU-modified epoxy-based membranes.

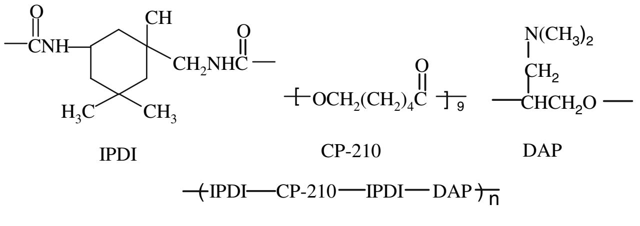
Experimental

Materials

Water-based epoxy resin (Xinlihua paint company, Tianjin, China) and tetraethoxysilane (TEOS) (Tianjin chemical company, Tianjin, China) were used without further purification. 3-Dimethylamino-1, 2-propanediol (DAP) was prepared in our laboratory. Isophorone diisocyanate (IPDI) (Bayor Co. Germany) was purified by vacuum distillation at 70 °C and 3.325 Pa. Poly(ε-caprolactoneglycol) (Cp-210, $M_n = 1{,}000$) (Solvay Interox, Australia) was degassed under vacuum (66.5 Pa) at 40 °C.

Preparation of SiO_2/PU composite particles

SiO_2/PU composite particles were prepared according to our previous report [8] by adding TEOS to a solution of PU, whose chemical structure is illustrated in Scheme 1, in THF with a mass ratio of 20:100, followed by acidification with hydrochloric acid and distillation of THF. The resulting emulsion contains SiO_2/PU nanocomposite particles with silica as the core and cationic PU as the shell.



Scheme. 1 Sequence of polyurethane and chemical structure of its components IPDI: Isophorone diisocyanate Cp-210: Poly(ε-caprolactoneglycol) DAP: 3-dimethylamino-1, 2-propanediol

Dispersing of SiO_2/PU nanocomposites in water-based epoxy resin

Aqueous emulsion of SiO_2/PU nanocomposites was added to water-based epoxy resin and mixed with strong agitation in bead mill for 6 h at room temperature.

Preparation of the electrophoretically prepared membranes

The electrophoretically prepared membrane was prepared by putting two iron sheets that acted as electrodes into the emulsions. When a voltage of 120 V was given between the two electrodes, the particles started moving towards negative electrode and depositing on its surface because the particles carry positive charges. The electrophoresis process was lasted for 2 min, and then the negative electrode was put into an oven at 170 °C for 0.5 h to be cross-linked by sealed isocyanate.

Characterizations

Particle sizes and size distribution in water were measured by BI9000 AL dynamic light scattering (BrookHaven CO., US), where an Ar type laser with wavelength 514.5 nm was used. The samples were firstly diluted with deionized water to a concentration of 0.5% m/m, followed by ultrasonic wave treatment to homogenize the emulsion.

Morphological observation of the electrophoretically prepared membrane was carried out by XL-30ESEM scanning electron microscopy (Philip, Holland).

XPS was performed on a PHI1600 (PE CO. US) with a hemisphere analyzer and a position sensitive detector. The spectrometer was equipped with a Mg/Kα(1253.6 eV) achromatic X-ray source operated at a power of 250 W. The spot size used was 1 mm × 3 mm. Survey scans were taken in the range of 0–1,100 eV. The spectrometer was typically run at the 6.67×10^{-7} Pa vacuum range.

Zeta potential was measured on Zeta PALS zeta potential analyser insruments (BrookHaven CO., US).

The physical properties such as thickness, hardness, tensile strength and throwing power (the coating ability of the electrophoretic coating to the areas far away from the negative electrode, such as concave areas or seams) were measured according to standards of CPA91-L131, GB6739-1996, HG2-1048-77 and GB13022-91. Salt-fog resistance, impact strength, elasticity and adhesive force were carried out by Salt-fog resistance box (Shanghai experiment instrument factory, Shanghai, China), Q-53-3K-1 coating impact instrument, QTX-1 coating elasticity instrument and QFZ-1 coating adhesive force instrument (Tianjin material experiment instrument factory, Tianjin, China).

Results and discussion

Effect of silica/PU nanocomposites on the size of epoxy resin particles

Figure 1 gives particle sizes and size distributions of PU, silica/PU, epoxy resin and silica/PU-modified epoxy resin in water. The average particle size of cationic PU is 40 nm, and its size distribution is quite narrow (Fig. 1a). After formation of silica in PU microcapsules (Fig. 1b), the average particle size becomes bigger (160 nm) and the particle size distribution wider. From the TEM miage of silica/PU nanocomposites, [8] the PU shell's thickness is estimated to roughly 25–50 nm. The average particle size of epoxy resin is 540 nm, with a wide size distribution ranging from 240 nm to 830 nm (Fig. 1c). After mixing with silica/PU nanocomposites (Fig. 1d), the average particle size decreases to 280 nm, and particle size distribution narrowed. In water, silica/PU nanocomposites exists as micelles with positive charges at the particle/water interface, and the particle sizes are much smaller than epoxy particles that have also positive charges on the surfaces. Because of the repulsion among positive charges, the introduction of smaller silica/PU particles can effectively prevent aggregation of epoxy particles. Therefore, silica/PU particles can not only disperse well in the epoxy resin, but also increase the dispersion of epoxy particles in water.

Effect of silica/PU nanocomposites on the zeta potential

Table 1 shows zeta potentials of PU, silica/PU, epoxy resin and silica/PU-modified epoxy resin. The introduction of silica does not change the zeta potential of PU at all. Because the information of silica is inside the PU particles, the amount of charges on the PU particles' surfaces is not been changed. However, after mixing with silica/PU nanocomposites, zeta potential of epoxy resin decreases from 166.30 mv to 143.20 mv, indicating that the further dispersion of silica/PU-modified epoxy resin in water can not only make the particle size smaller, but the surface charge of the particles reduce.

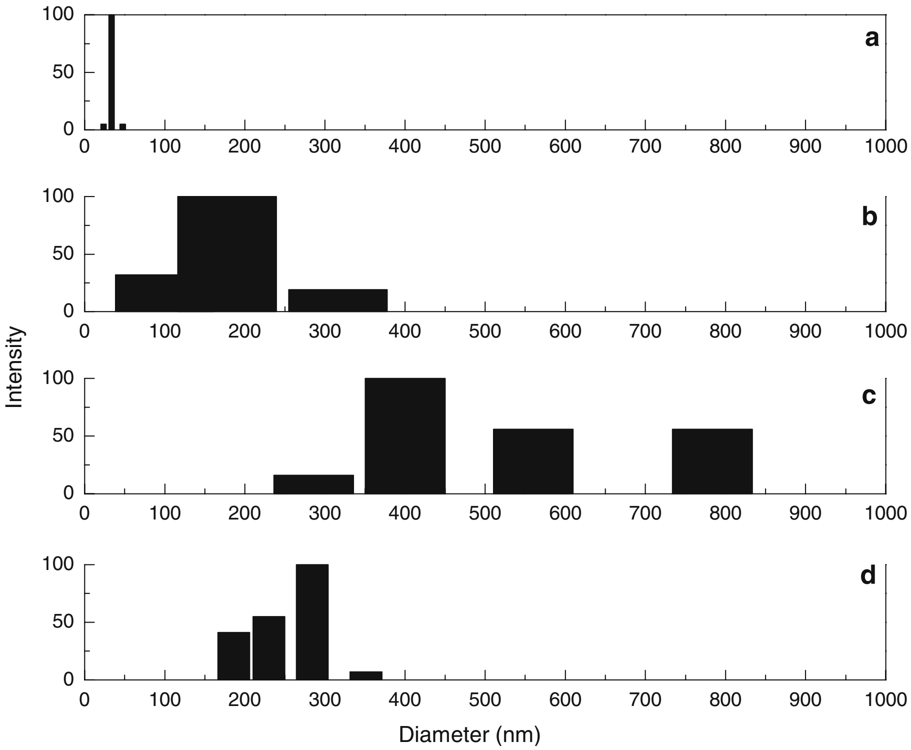


Fig. 1 The particle sizes and distributions (**a**) PU (**b**) SiO_2/PU nanocomposites (**c**) epoxy resin (**d**) SiO_2/PU nanocomposites-modified epoxy resin

XPS analysis of the electrophoretically prepared membrane

In order to check the co-electrophoresis of epoxy particles with silica/PU particles, the surfaces of the electrophoretically prepared membranes with and without silica/PU nanocomposites were analyzed by XPS. The spectra are shown in Figure 2 and 3. Compared to epoxy resin, signal of Si appears at 103.1 eV for silica/PU-modified epoxy membrane, proving existence of silica in the electrophoretically prepared membrane. Silica alone can't be electrophoresed because there is not any charge on its surface. As mentioned above, silica is encapsulated by cationic PU, and thus can be brought to the negative electrode when silica/PU particles move to the electrode during electrophoresis process. Another new signal at 399.9 eV, assignable to *N*, was observed in the spectrum of silica/PU modified epoxy membrane. The signal of *N* is not detectable in epoxy membrane, because *N* exists as quaternary cations in epoxy resin coating, which deposits to the negative electrode and presents at the inner surface of the membrane, and consequently not be detected. As to silica/PU-modified epoxy resin, the *N* atoms of the urethane bonds in the hard segment of PU could be on the outer surface of the membrane due to lack of positive charges and thus can be detected by XPS.

From XPS analysis, an increase of carbon content from 49.6% m/m to 52.3% m/m and a decrease of oxygen content from 50.4% m/m to 42.8% m/m were also observed when silica/PU was incorporated into the epoxy resin. This seems reasonable because PU contains more carbon and less oxygen than epoxy resin.

SEM observation of the electrophoretically prepared membranes

Table 1 Zeta potentials

sample	1	2	3	4
zeta potential/mv	120.45	121.20	166.30	143.20

sample 1: PU 2: SiO_2/PU nanocomposites 3: epoxy resin 4: SiO_2/PU nanocomposites-modified epoxy resin

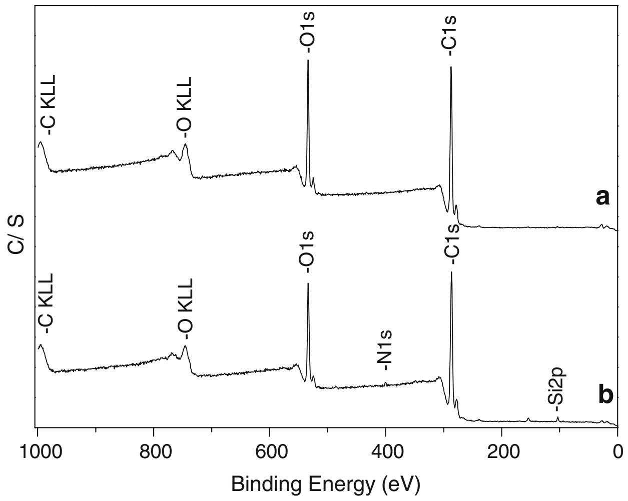


Fig. 2 XPS wide scan spectra of electrophoretically prepared membranes of epoxy resin (**a**) and SiO_2/PU nanocomposites-modified epoxy resin (**b**)

The properties of the membranes are related to their morphology. Thus, SEM is used to study the surface morphologies of the epoxy-based electrophoretically prepared membranes with and without silica/PU nanocomposites along with those of PU and silica/PU electrophoretically prepared membranes. The images are shown in Figure 4. Microphase domains were observed in all four membranes with the smallest size in PU membrane (20 μm) and largest size in epoxy membrane (300 μm). The order of the domain sizes is the same as those of the particle sizes and size distributions in the corresponding emulsions before electrophoresis. This means that the domain size is related to the particle size and size distribution in the emulsion for electrophoresis. When particle sizes are small and their distribution is narrow, such as the case of PU, the electrophoresis rates of individual particles are big and almost the same, and thus all the particles deposit on the electrode with a very narrow time gap and the tendency to form aggregates during electrophoresis is minimum. As a result, a homogeneous membrane is formed upon curing.

On the contrary, when particle sizes are big and their distribution is wide, such as the case of epoxy resin, the electrophoresis rates of individual particles are different, small particles arrive to the electrode first, and big particles arrive later. During electrophoresis, big particles have a strong tendency to form aggregates because they stay longer in the electrophoresis emulsion. Upon curing, the molecules in big aggregates are harder to rearrange for crosslinking reaction, and consequently the degree of crosslinking is lower, and loose piles are formed. This explains why the size of microphase domain is the biggest in epoxy membranes.

As discussed earlier, silica/PU nanocomposites can improve dispersion of epoxy resin, both particle sizes and size distribution are significantly reduced. Therefore, the size of microphase domain in silica/PU-

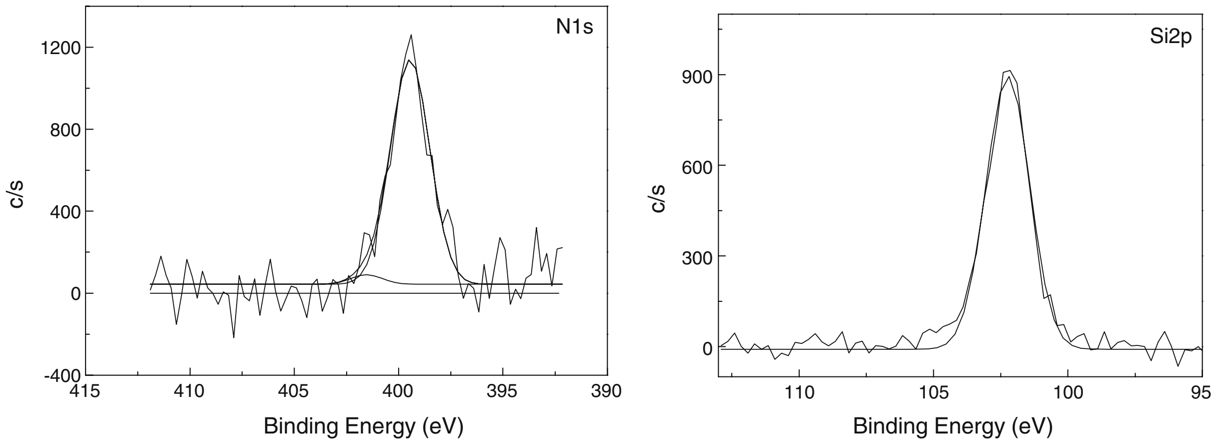


Fig. 3 XPS spectra of N and Si in electrophoretically prepared membrane of SiO_2/PU nanocomposites-modified epoxy resin

modified epoxy membrane is much smaller compared to that in the unmodified epoxy membrane.

Properties of the electrophoretically prepared membranes

The properties of silica/PU-modified epoxy membrane are investigated and compared with those of unmodified and PU-modified epoxy membranes. The results are listed in Table 2. Most of the measured properties have been improved. The tensile strength, hardness and salt-fog resistance increase significantly due to the presence of rigid silica particles in the membrane. In general, the addition of rigid particles to polymer matrices can improve the strength, hardness and dimensional stability at a sacrifice of toughness. However, as shown by impact strength, the toughness of silica/PU-modified epoxy membrane is increased by 11% compared to the unmodified epoxy membrane. This is because silica is encapsulated by PU which is a very tough material.

The improved properties are also related to the strong interfacial interactions between silica and PU and between PU and epoxy due to hydrogen bonding and participation in crosslinking reactions. The carbonyl groups (in urethane and ester structures) of PU can form hydrogen bonds with both silanol groups of silica and hydroxyl groups of the epoxy resin. The NH (in the urethane structure) and end hydroxyl groups of PU can react with the crosslinker during curing, and thus PU is covalently linked to the epoxy resin network.

Fig. 4 Scanning electron microscope images of electrophoretically prepared membranes (15,000 times) (**a**) PU (**b**) SiO_2/PU nanocomposites (**c**) epoxy resin (**d**) SiO_2/PU nanocomposites-modified epoxy resin

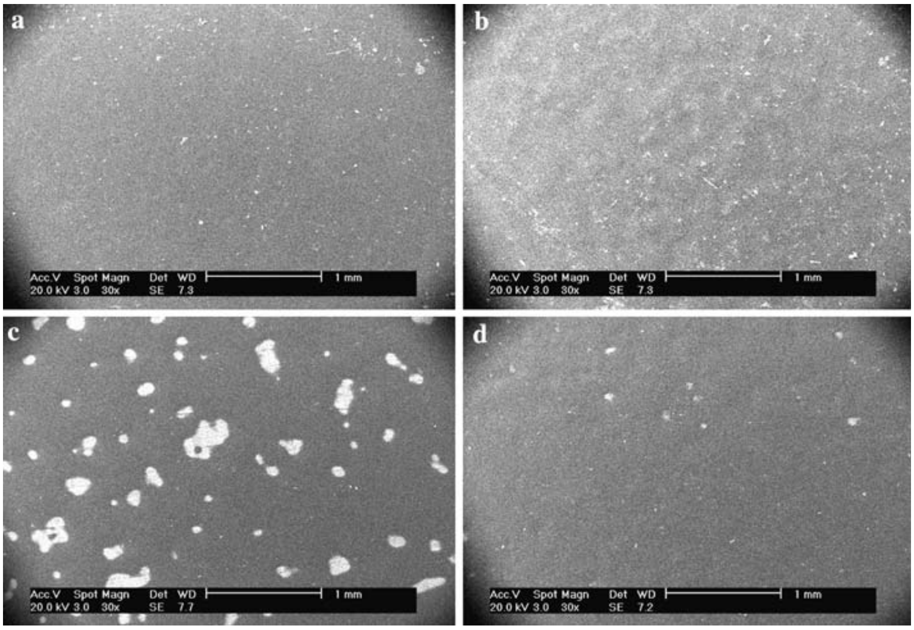


Table 2 Properties of the electrophoretically prepared membranes

sample*	impact strength/ kg mm	elasticity/ mm	adhesive force/ level	hardness/ *H***	salt-fog tolerance/days	thickness/ μm	tensile strength/ Mpa	throwing force/%
1	450	1	2	2	30	18 ± 2	46.760	70
2	500	1	2	3	30	20	48.241	70
3	500	1	1	4	50	24	70.474	80

* sample 1: epoxy resin 2: epoxy resin modified by PU 3: epoxy resin modified by SiO_2/PU nanocomposites ** *H*: the hardness of penciles in pencile test

Conclusion

Silica/PU nanocomposites synthesized by in situ formation of silica from tetraethoxysilane (TEOS) in cationic polyurethane microreactor can co-electrophoresed with epoxy resin, and thus is useful in modification of epoxy-based the electrophoretically prepared membrane. A better dispersion of epoxy particles in the electrophoretic coating have been achieved and as a result, the surface morphology have shown much smaller microphase domains, favoring improvement of the membrane properties. Most of the measured properties of the electrophoretically prepared membrane have been in deed improved by incorporation of silica/PU nanocomposite. Because rigid silica is encapsulated by tough PU, the strength and toughness of the membrane have been simultaneously improved.

The successful use of silica nanoparticles in modification of epoxy-based electrophoretic coating can be attributed to their encapsulation by cationic PU, which brings silica to the electrode during electrophoresis, effectively prevent aggregation of primary silica particles, and increase toughness of the membrane. This work could be of interest for the electrophoretic coating industry.

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