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High-grafted Surface Modification of Silica Gel Particles with Urushiol

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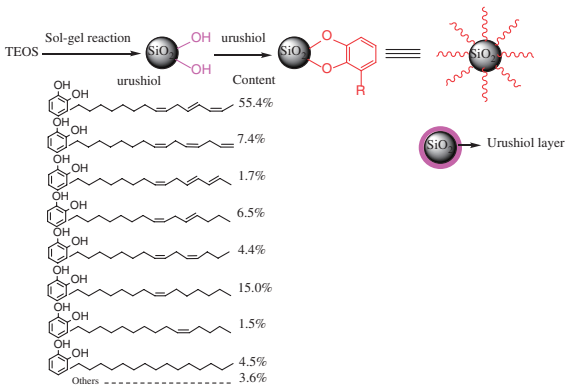
A facile method for high-grafted surface modification of silica gel particles was developed in this paper. Silica gel was obtained by traditional avenue and then reacted with urushiol (Chinese lacquer). The obtained product was characterized by FT-IR, elemental analysis, TGA, SEM, and EDX. The results suggested that the reaction occurred between silica and urushiol and that the grafting ratio added up to 15.35 ± 0.05 wt %. The result of EDX demonstrated that the urushiol moieties were mainly on the surface of silica particles. Additionally, the as-prepared silica particles had good dispersion.

Silica is a traditional inexpensive inorganic ingredient as a filler to improve mechanical and thermal properties of polymers and polymer composites in the polymer industry.[1–6] At the same time, it is necessary that the silica particles should be homogeneously dispersed in the polymer matrix to obtain good properties for the composites. However, high surface energy makes silica particles generally extremely unstable, liable to undergo chemical reactions with the environment and also to self-aggregate.[1] Many routes have been introduced to settle this problem including polymer adsorption by wrapping,[7] ex situ[8] or in situ[9–12] polymer-assisted fabrication, and surface modification.[13,14] To exhibit outstanding properties, surface modification is an effective way to avoid phase separation and to keep homogeneously dispersive characteristics. Alkyl silane coupling agents have been widely used to modify inorganic particles,[15–19] e.g., silica particles. However, they are mainly obtained from chemical synthesis.

In this paper, a natural modifier,[20] urushiol (Chinese lacquer), was presented to modify silica particles. We made use of the hydroxy groups on the phenyl ring of urushiol reacting with silanol (Si–OH) groups on the surface of silica particles to accomplish high-grafted surface modification of silica particles. Compared with the traditional modification routes by using alkyl silane coupling agents, the present method used a natural product as a coupling agent to modify silica particles with high-grafted organic moieties.

Silica gel particles were prepared by hydrolysis of TEOS with ammonia according to the Stöber method.[21] The reaction between the hydroxy groups on the phenyl ring of urushiol and silanol (Si–OH) groups has been already clarified.[22–26] In a typical experiment, 10 wt % absolute ethanolic urushiol solution was added to silica gel in a 100-mL flask under rapid stirring at 80 °C and reacted for 30 min, in which the mol ratio was 1:0.1 (*n*(TEOS):*n*(urushiol)), and the reaction occurred between silanol (Si–OH) groups and the hydroxy groups on the phenyl ring of urushiol to obtain soil-gray product. The modified products were centrifuged and washed with absolute ethanol under ultrasound to remove soluble materials, and the process was repeated thrice. Finally, the soil-gray products were dried at 80 °C for 6 h. The overall reaction of the modification is schematically shown in Scheme 1.



Scheme 1. Schematic high-grafted surface modification of silica particles with urushiol.

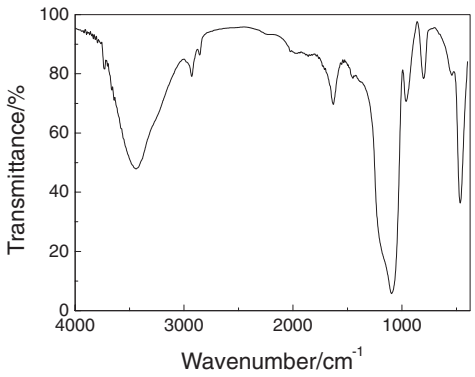


Figure 1. FT-IR spectrum of high-grafted surface modification of silica particles with urushiol.

The surface modification of silica particles was further confirmed by FT-IR (Figure 1) (Nicolet5700 FT-IR spectrometer, America–Switzerland) and TGA (Figure 2) (Mettler TGA/SDTA851 thermogravimetric apparatus, Switzerland, Mettler-Toledo Inc.). The peak at 1630 cm^{-1} in Figure 1 was assigned to the C=C bond stretching vibration of the side chain on the phenyl ring of urushiol; the peaks at 2936 and 2852 cm^{-1} were the C–H stretching vibration of $–CH_3$ and $–CH_2–$ groups, respectively. The amount of urushiol moieties on the silica particles was estimated to be 15.29 wt %, based on the carbon content (12.27 wt %) of the modified silica (vario EL III Elemental Analysis, Elementar Inc., Germany), and to be 15.40 wt %, based on the TGA data of the modified silica. The result of EDX demonstrated that the urushiol moieties were mainly on the surface of silica particles (Figure 3). The

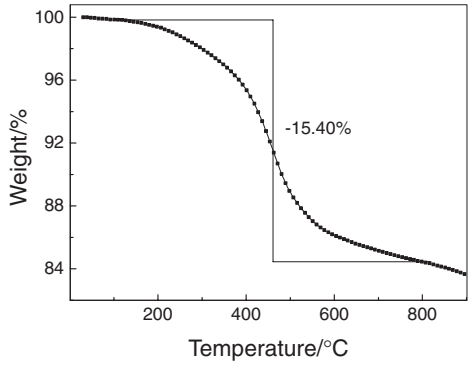
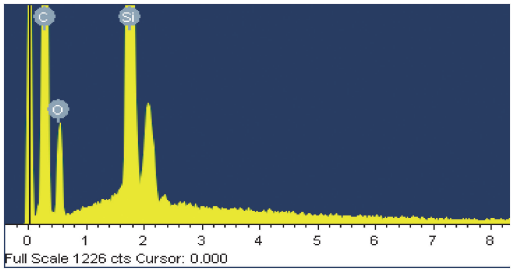


Figure 2. TGA curve of high-grafted surface modification of silica particles with urushiol.



Element	Weight/%	Atomic/%
C	80.34	86.78
O	11.87	9.63
Si	7.79	3.60
Totals	100.00	

Figure 3. EDX spectrum and surface elemental analysis of high-grafted surface modification of silica particles with urushiol (Scanning area: ca. 100 nm × 100 nm on the surface of a single modified silica particle).

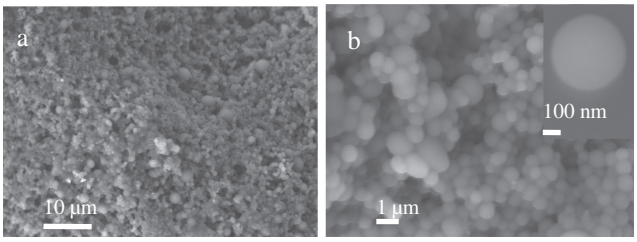


Figure 4. SEM images of high-grafted surface modification of silica particles with urushiol. (a) Low-magnification image, (b) high-magnification image and a single modified silica particle with a diameter of about 300 nm (inset).

morphology of the modified silica was investigated using scanning electron microscopy (JSM-7500F equipped with an Oxford Inca EDX analyzer). Figure 4 indicates that the morphology of the modified particles is approximately spherical with a diameter of about 300 nm, and good dispersion was also observed. All these results clearly proved that the as-mentioned approach was an effective technique to graft urushiol moieties onto the silica particles.

In conclusion, high-grafted surface modification of silica particles with urushiol was accomplished by using silica gel as precursor. The urushiol moieties were found to be highly adhesive to the surfaces of silica particles, with quantitative EDX analysis providing useful insight into the bonding behavior. Because urushiol is a trisubstituted catechol derivative with a long aliphatic unsaturated side chain which could be compatible with nonpolar or low-polar polymer or be copolymerized with the prepolymer, the as-prepared silica particles have potential for use in polymeric industry.

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