Preparation of hydrophobic thin films based on PTFE/acrylic resin/SiO_2 complex

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Hydrophobic and oleophobic repellency are highly desirable for numerous everyday applications, e.g. aerospace, lithography, sports and outdoor clothing, biomedical layers, integrated sensors, and protection against environmental fouling, etc. [1–6]. Fluorinated polymers exhibit extremely low surface free energy and are used as important raw materials for surface modification agents such as water-and-oil repellents, lubricants, and surfactants. Polytetrafluoroethylene (PTFE) is a commercially available material with outstanding thermal stability, good resistance to solvents, and low friction coefficient, and has been widely used as an engineering plastic. However, PTFE shows high wear rate at normal friction conditions and cold-flow phenomenon under load, and it is not easy to process because of its nonsolubility and high melting point. A considerable effect has been made to improve the processing properties [7]. Transparent hydrophobic films have been a focus of interest in recent years [8]; however, transparent hydrophobic films based on PTFE are rare. In this letter, water dispersible PTFE was used to prepare transparent hydrophobic PTFE containing acrylic resin/SiO_2 complex coatings.

To prepare acrylic resin/SiO_2 complex emulsion, acrylic monomers, methylmethacrylate (MMA), butyl acrylate (BA), and styrene (St) (25:15:5, weight ratio) were emulsion polymerized in the presence of silicon sol with a diameter of SiO_2 particle of 10–20 nm, 10 wt% of SiO_2 of the monomers used, and using 3-trimethoxysilyl propyl methacrylate (TMSM) as a cross linking agent. The water dispersible PTFE, with PTFE particles less than 200 nm, was added to the hybrid emulsion described above. The complex emulsion was sprayed onto glass, tinplate substrates, dried at room temperature for 30 min, heat treated at 120 °C for 3 hr, then polished with soft cotton toile. Hydrophobic films prepared as described above are transparent although look slightly opaque.

Table I shows the main items of the complex emulsion as prepared. TG/DTA analysis shows that the hybrid resin prepared without addition of PTFE has a good thermal stability. The thermo decomposition temperature of the hybrid material is higher than 345 °C. The water repellence of the hydrophobic PTFE containing film was determined using contact angle measurements on a JY-82 contact-angle meter (China). For the water droplet, distilled deionized water was used, 50 μL in volume. Contact angles reported were average of five different spots measurements. The water contact angle on complex film prepared by increased dramatically from 35 ° to 93 ° with only a small addition of PTFE of about 5 wt%. Addition of 8 wt% of PTFE makes the water contact up to 110 °, which is almost the same as that of a pure PTFE film (108 °).

To make transparent PTFE containing films, the emulsion was diluted with water, and sprayed onto glass substrate. The thickness of the target film can be controlled by adjusting the spraying duration and is determined to be less than 2 μm by measuring through a cross-sectional SEM image to an accuracy of $\pm$0.1 μm. Thickness less than 2 μm can be fabricated through this processing. This thin film is transparent though looks slightly opaque. UV absorption spectrum of the complex film was recorded on a He λ ios α (UNICAM Co.) ultraviolet–visible light spectrophotometer (Fig. 1), using uncoated glass substrate as a reference. The transmittance of visible light of the complex thin film is very high, with only a little decrease compared with glass substrate.

The surface and cross-section morphology of the complex film were observed in a JSM-5600 scanning electron microscope (SEM) and the experimental results are given in Fig. 2. The top view of the film shows that continuous film has been fabricated on the substrate surface, with a fine smooth surface. The

TABLE I Specification of the complex emulsion

Items	Index
Appearance	White emulsion
Solid content wt%	20%
pH value	8–10

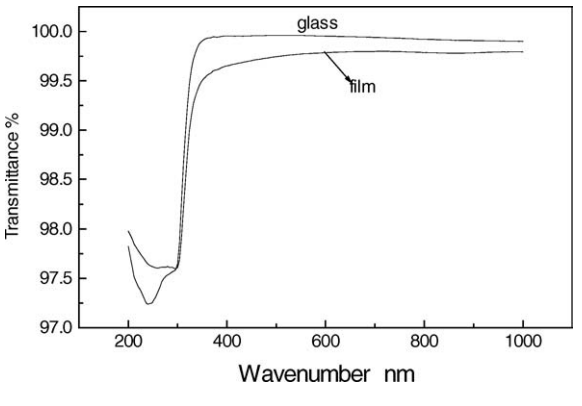

Figure 1 UV absorption spectrum of the complex film.

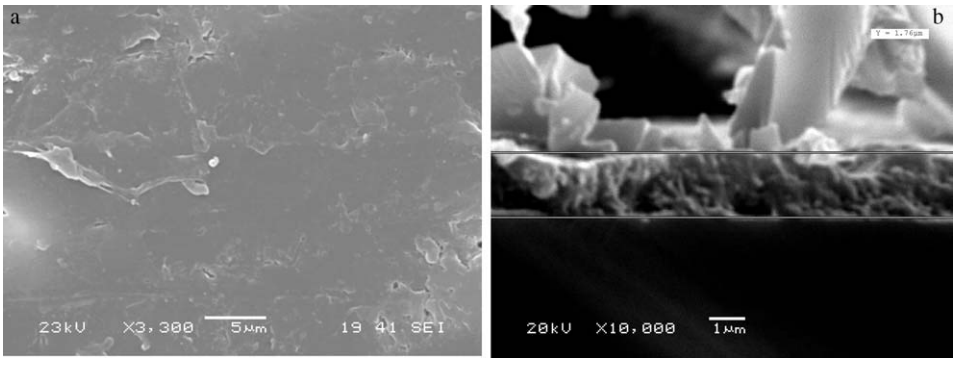

Figure 2 SEM images of the complex film (a) top view and (b) cross section (thickness, 1.8 μm).

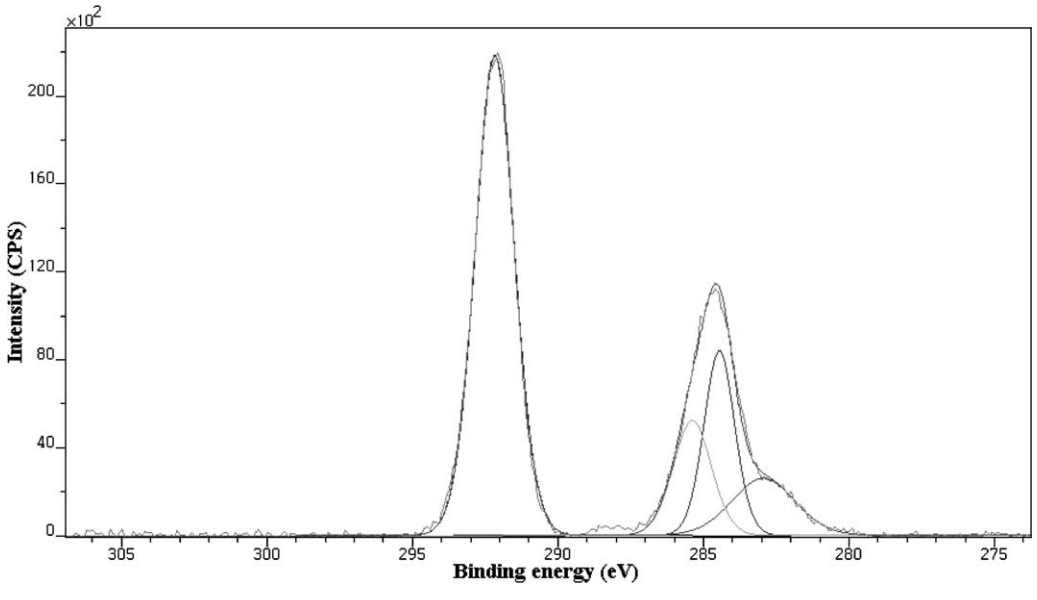

Figure 3 C_{1s} XPS spectrum of the complex film surface as prepared.

cross-section SEM image indicates a uniform thickness of about 1.8 μm of the film.

To confirm the existence of PTFE on the surface layer of the complex films as prepared, X-ray photoelectron spectroscopy (XPS) spectrum was obtained on an axis ultra-multi-technique electron spectrometer (Kratos, UK) with an Al K_α X-ray source and a pass energy of 40 eV. The Al anode voltage was 15 keV and the filament current was 20 mA. The pressure in the spectrometer during analysis was typically in the 10^{-9} Torr range. Using a least-squares curve fitting program installed in the spectrometer, the C_{1s} for the complex film surface was split into several subpeaks of functional groups, and the concentrations of functional groups for the complex film surface were obtained. A typical splitting of the spectrum of C_{1s} is shown in Fig. 3. The peaks in the spectrum can be ascribed to groups as follows, CF at 292.2 eV, C=O at 285.4 eV, CH at 284.5 eV, and C at 282.9 eV can be assigned to contaminant carbons, as shown in the spectrum. From the C_{1s} spectrum of the complex film surface, about 53% C atoms are CF_2 (estimated according to the ratio of areas of peaks), indicating the aggregation of PTFE near the outmost surface layer.

To examine the adhesion of the complex film with metal substrate, thin films were prepared on tinplate substrate using the method described above. The adhesion was evaluated by orthogonal cross-course adhesive tape experiments according to ASTM D3359 (method B). The film obtained shows a great adhesion of 5B. The flexibility of the complex film was examined according to the Chinese Standard Test (GB/T 6742) which is commonly used to evaluate the flexibility of coatings. The experimental results show that the film prepared has extremely good flexibility and bending flexure. The impact endurance test of the film was carried out according to the method described by Chinese Standard Test (GB/T 1732) which is commonly used to evaluate the impact resistance of coatings, and the complex film shows an excellent impact resistance of 50 cm. This indicates that the film prepared has good mechanical properties, and a promising future.

Acknowledgments

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