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Tailoring the wettability of polypropylene surfaces with halloysite nanotubes

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ABSTRACT

In this contribution, halloysite nanotubes (HNTs), a kind of natural hydrophilic nanoclay, are incorporated into polypropylene (PP) for tailoring the surface microstructures of the composites prepared by solution casting. HNTs act as heterogeneous nuclei for PP, which leads to the change of phase separation process during drying of the composites and consequently the microstructures of composite surfaces. Micropapilla like hybrid spherulites with nanostructures are formed on the PP/HNTs composite surfaces. The rough surfaces demonstrate superhydrophobicity with a maximum water contact angle as nearly 170° and sliding angle of about 2°. The spherulites size, surface roughness, and wetting property of PP can be tuned by HNTs. HNTs can significantly improve the thermal degradation behavior of the composites which is attributed to the well-dispersed HNTs and the improved interfacial interactions by the nucleation effect. The present work provides an alternative routine for preparing polymer superhydrophobic surfaces via tailoring the surface microstructures by adding nanoparticles in a solution process.

1. Introduction

Superhydrophobic surface has attracted widely interests all over the world in recent years with evidence of the rapid increasing numbers of published papers on this issue [1–9]. This can be attributed to the unique wetting properties of these surfaces, such as extreme water repellency and self-cleaning. A water droplet on superhydrophobic surfaces keeps almost as a spherical shape with a contact angle larger than 150° and it can easily roll off when the surfaces are tilted. If there are dust on these surfaces, the rolling water droplets can bring them off and hence the surfaces can keep always clean. In nature, many plant and insects, such as lotus leaves [2], water strider's legs [7] and butterfly wings [10], exhibit surfaces with the superhydrophobic property. Generally, wettability of a solid is governed by both the chemical composition and geometrical microstructure of the surfaces. To mimic the topology of the natural water-repellent surfaces, artificial superhydrophobic surfaces are prepared by vast different techniques and materials [8,9]. These synthesized surfaces with unique wettability can be applied in many areas, such as the prevention of the adhesion of snow to antennas and windows, self-cleaning traffic indicators, antifouling coatings, the reduction of frictional drag on ship hulls, metal refining, stain-resistant textiles and cell motility. Although these artificial superhydrophobic surfaces are reported with excellent water-repellent property, most of them suffer from the drawbacks such as complicate procedures, expensive raw materials, and non-reproducible results. Therefore, exploiting a simple, flexible, and economic method for superhydrophobic surfaces is generally highlighted.

In 2003, Erbil et al. reported a simple approach for forming superhydrophobic surfaces with polypropylene (PP) via controlling phase separation by adding non-solvent [6]. The non-solvents act as precipitator to promote the phase separation process when PP solution is drying. Formation of porous surface with finer spherulites is found and the microstructures and wettability of the PP surfaces can be tuned by the non-solvents. Inspired by this result, other polymers such as polyethylene (PE) [11–13], polycarbonate (PC) [14,15], polystyrene (PS) [16], poly(vinyl chloride) (PVC) [17], and poly(L-lactic acid) (PLA) [18] were employed for fabrication of superhydrophobic surfaces using the controlled phase-separation method. For example, phase separation process can be induced by the non-solvents of ethanol, water or their mixtures and superhydrophobic surfaces of PE, PS, PC, PVC, or PLA are obtained. The non-solvents act as "seed" where the polymer chains tend to be absorbed in the phase separation process. For crystalline polymer systems, the role of non-solvents is like nucleation which can leads to the alignment and entanglement of polymer chains on the surfaces of nuclei. Although organic solvents are involved in the phase-separation method, it is a simple, effective, and flexible routine for fabrication polymer superhydrophobic surfaces. Recently, Rioboo et al. investigated the effect of the solution concentration and film thickness on the superhydrophobicity of various PP in detail [19]. However, such kinds of technologies were confined to neat polymers and never implemented in polymer composites.

Nanoparticles, such as carbon nanotubes (CNTs), nanoclays, and nanosilica, are incorporated into polymers for improving their performance or functions [20]. The introduction of nanoparticles can

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significantly change the microstructures of polymer matrix which in turn leads to the changed properties of polymer materials. The nucleation of nanoparticles towards crystalline polymers is widely concerned due to their significance for both theoretical and practical values. For example, CNTs can induce transcrystalline or shish-kebab crystal of polyolefin via soft-epitaxy mechanism under proper condition [21,22]. Clay or nanosilica can also play the heterogeneous nucleating points role for various polymers [23–25]. Generally, the nucleation effect of nanoparticles results in finer crystals, faster crystallization process, and some times novel crystal forms. When the polymer composites are prepared by solution blending method, nanoparticles can accelerate the phase separation process during drying of the composites via nucleation. As a consequence, rough polymer surfaces can also be formed when one replaces the non-solvent with nanoparticles as nanoparticles can act as a special precipitator of polymer solutions. In the present paper, we used a kind of natural occurred inorganic nanotubes, halloysite nanotubes (HNTs), to tailor the surface microstructures of PP in a solution process. The heterogeneous nucleation of HNTs to PP was examined. Micro-papilla like hybrid spherulite with nanostructures was observed for the PP/HNTs composite surfaces. These rough surfaces demonstrate superhydrophobicity with a water contact angle higher than 160° and sliding angle less than 10°. The present work provides an example for tailoring the surface microstructures and wetting property of polymers by adding nanoparticles in a solution process.

2. Material and methods

2.1. Materials

Isotactic PP granules with tradename F401 were commercial products of Lanzhou Petrochemical Co. Ltd. The melt flow index was determined as 2.84 g/10 min (after ISO-1133: 1997(E)). The HNTs were mined from Yichang, Hubei, China. The elemental composition was determined by X-ray fluorescence (XRF) as follows (wt.%): SiO_2, 58.91; Al_2O_3, 40.41; Fe_2O_3, 0.275; TiO_2, 0.071. The Brunauer–Emmett–Teller (BET) surface area of the used HNTs was 50.4 m^2/g. HNTs were purified according to the Ref. [26]. The purified HNTs were with highly tubular morphology as shown in Fig. 1.

2.2. Methods

2.2.1. Preparation of PP/HNTs composites superhydrophobic surfaces

The superhydrophobic surfaces of PP/HNTs composites were prepared via solution casting method. A typical procedure was as follows: 0.6 g PP granules were dissolved completely in 30 mL xylene at 120 °C. Then dried HNTs powders were added to the solution under stirring and the temperature was kept at 120 °C. The PP/HNTs solutions were stirred for 30 min with a rotation rate of 800 rpm to completely disperse HNTs. Finally the solutions were casted on clean glass slides and dried at room temperature for 1–4 h. The final thickness of the formed film was around 50 μm. The content of HNTs was the weight ratio of HNTs to the total composites.

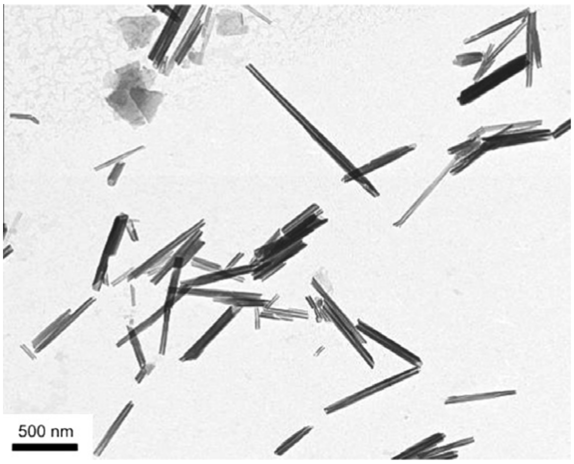

Fig. 1. Transmission electron microscope image of the used HNTs.

2.2.2. Characterization

Differential scanning calorimetry (DSC) data of neat PP and PP/HNTs composites were measured by TA Q20 using nitrogen as the purging gas. The samples were heated to 210 °C at the ramping rate of 40 °C/min. The samples were kept at 210 °C for 5 min to eliminate thermal history before they were cooled down to 40 °C at rate of 10 °C/min. The exothermic flows were recorded as a function of temperature. The crystallization onset temperature ($T_{c\ on}$) and peak temperature (T_c) were obtained from the curves by the TA Universal Analysis software.

The X-ray diffraction (XRD) patterns of PP and PP/HNTs composites were recorded by the Bruker D8 Advanced X-ray Diffractometer. The Cu Kα radiation source was operated at 40 kV power and 40 mA current. The patterns were recorded by monitoring those diffractions that appeared from 2° to 40°. The scanning speed was 1°/min.

The morphologies of the crystallites of PP and PP/HNTs composites were recorded with an Olympus BX41 polarized optical microscopy (POM). The PP and PP/HNTs composites thin films for POM observation were obtained by dropping their diluted solutions on clean glass slides and subsequently drying them in air.

The scanning electron microscopy (SEM) micrographs were taken with LEO1530 VP SEM machine. The samples were coated with a very thin layer of gold before observation.

To evaluate the effect of HNTs on the phase separation process, the weight loss experiments were performed. About 0.25 g PP solution or PP/HNTs solution was carefully dropped on glass slide which was placed on a balance. The initial weight was recorded. Due to the gradually evaporation of solvent, the weight decreased and the changed weights were recorded every 30 s. The initial concentration of the PP solution and PP/HNTs solution was same for comparing the total drying time.

To evaluate the surface roughness of PP and PP/HNTs composites, roughness measurement were performed using a BMT Expert3D analyzer. The 3D surface topography of the samples was recorded on the basis of the white-light interference theory. The scanning area for all the samples is 4 × 3 mm. The scanning point density was 300 point/mm. The area average roughness (S_a) for all the samples were obtained using the BMT measurement and evaluation software.

Water contact angle and sliding angle of the prepared surfaces were measured with KRUSS Drop Shape Analyzer DSA 100 instrument under room temperature. The data measurement of contact angle and slide angle for all the samples were repeated for five times to obtain reliable values. The volume of water droplet was 4 μL for the contact angles measurement. The contact angles were calculated by software according to the Laplace-Young model. The sliding angle values were the critical angle of the inclination of the surfaces when a 10 μL water droplet started to roll off.

XPS spectra of the PP/HNTs composites with 15% HNTs and 40% HNTs were recorded by Kratos Axis UltraDLD with an Aluminum (mono) Kα source (1486.6 eV). The atom ratio values were calculated by integration of the area for the corresponding peaks by software.

Thermogravimetric analysis (TGA) for all the samples were carried out under air atmosphere with TA Q5000 at a heating rate of 10 °C/min from room temperature to 600 °C.