Electronic Supplementary Information(ESI) for

Rod-Like Attapulgite/Polyimide Nanocomposites with Simultaneously Improved Strength, Toughness, Thermal Stability and Related Mechanisms

Li An, Yongzheng Pan, Xiwen Shen, Zhaoqiang Zhang, Hongbin Lu* and Yuliang Yang*
Key Laboratory of Molecular Engineering of Polymers, Ministry of Enducation & Department of Macromolecular Science, Fudan University, Shanghai, 200433, China

Experimental Section

1. Materials

4, 4'-Oxydianiline (ODA, purity: 98%) and pyromellitic dianhydride (PMDA, purity: 98.5%) were purchased from Sinopharm Co. Shanghai and used as received. Attapulgite (Attagel 50, average particle diameter: 0.1 µm) were purchased from Engelhard Co.,USA. 4,4'-methylenebis(phenylisocyanate) (MDI, purity: 98%) was purchased from Aldrich Chemical Co. and used as received. N,N-dimethylformamide(DMF) was vacuum distilled over anhydrous magnesium sulfate. All other reagents and chemicals were of analytical grade and used as received.

2. Preparation of ODA-modified ATT

Attapulgite (ATT) clay was firstly purified with sodium hexametaphos-phate solution to remove iron ions and other more dense impurities such as quartz by sedimentation. The supernatant suspension was recollected by centrifugation. The purified ATT was then activated in 5M HCl solution at 80 °C for 1 h to remove the residual carbonates and introduce more hydroxyl groups on the surface. After exhaustively washed to pH neutral with water, the activated ATT were dried at 150 °C in vacuum for 12 h to remove any water from the external surfaces. The dried ATT (5g) was ground and re-dispersed in dry DMF to form 5 wt % suspension by using a high shear homomixer and ultrasonication for 30 min. MDI (0.01mol) solution in DMF was added to the stirred suspension of ATT. The reaction was maintained at 80 °C under nitrogen for 1 h. After washed twice with DMF, a solution of ODA (0.05mol) in DMF was added, and stirred overnight at 55 °C. After the reaction, modified ATT was collected by centrifugation at 6000 rpm. To completely remove ungrafted molecules and bulk polymer, ATT was washed sequentially with DMF, water and acetone. The obtained ODA-modified ATT was then dried in vacuum and ground.

3. Preparation of ATT/polyimide nanocomposites

Poly(amide acid) from PMDA and ODA was prepared as follows: ODA (10.0 mmol) was first dissolved in DMF in a three-necked flask equipped with nitrogen inlet and mechanical stirrer at room temperature with continuous stirring. After ODA was completely dissolved, PMDA (10.1 mmol) was added to the flask in 3 batches with an interval of 30 min between batches. The mixture was stirred vigorously for 24h to form a viscous but transparent poly (amide acid) solution.

To prepare ODA-modified ATT suspension in DMF at different concentrations, different quantities of organo-ATT were added to 10g DMF and then each was mixed for 1h under high shear. The ATT suspensions were subsequently mixed with the PAA solution under vigorously stirring for another 12h to obtain ODA-modified ATT/ poly (amid acid) in DMF. The final solid content of poly (amid acid) in DMF is 11%. The poly (amid acid)/ATT solutions with different ATT loadings were then used to cast films on glass slides. The films were placed in a vacuum oven at room temperature to remove the air bubble and then were thermally treated respectively at 80 °C for 3h, 100 °C for 2h, 150, 200 and 300 °C for 1h under N_2 to completely remove the solvent and achieve imidization.

4. Characterization and Measurements

Fourier transform infrared spectroscopy (FTIR, Nicolet Magna-550 spectrophotometer) was used to study the covalent bonding of organic molecules to the ATT surface, where the ATT powder was dispersed in KBr disks and experiments were conducted over the range 400 ~ 4000 cm^{-1}. The morphologies of original ATT nanorods and nanocomposites were inspected using scanning and transmission electron microscope (SEM, Tescan 5136MM, and TEM, Hitachi H-600). To examine the dispersion state of nanorods in polyimide, the nanocomposite film was fractured in liquid nitrogen, etched in sulfuric acid and then coated with gold for SEM observations. The sample preparation for TEM experiments followed an epoxy encapsulation procedure and then the encapsulated nanocomposite film was cut with an ultramicrotome at room temperature. For characterization of the fracture surface of the neat polyimide and nanocomposite films, the samples obtained after completing tensile tests were directly mounted on the carbon tape and then coated with gold for the SEM observation of surface morphology. Utraviolet-visible spectrometer (UV-vis, Perkin-Elmer Spectrometer Lambda 35) was used to examine the effect of ATT nanorods on the light transmittance of polyimide films. For each sample three different places were randomly chosen for wavelength scanning, which indicates the dispersion state of ATT nanorods in polymer.

Thermogravimetric analysis (TGA, Perkin Elmer, Pyris 1) was employed to determine the amount of organic molecules grafted on the ATT surface and the thermal stability of ATT/polyimide nanocomposites. The TGA scans for ATT nanorods were performed in the range of 50 ~ 700 °C with a heating rate 10 °C /min while for the nanocomposites the TGA scans were conducted in a range of 100 ~ 800°C with heating rate 20 °C /min. All scans were completed in a nitrogen atmosphere. The dynamic mechanical analyses (DMA, Netzsch DMA242 analyzer) of the polyimide and nanocomposite films was performed from 25 to 400 °C with a heating rate 5 °C /min and frequency 0.1Hz. The tensile strength, modulus and elongation at break of the nanocomposite films were obtained on an Instron-5565 universal testing system at a crosshead speed of 2 mm/min for effective sample length of 20mm at room temperature. The tensile properties of each sample were determined from an average of five tests.