Preparation and Characterization of Sustainable Polymer Nanocomposites Based on Surface Modified Halloysite Nanotubes

景,慧

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氏 名:景 慧

論文題名: Preparation and Characterization of Sustainable Polymer Nanocomposites Based on Surface
Modified Halloysite Nanotubes

表面修飾ハロイサイトナノチューブを用いた環境調和型高分子複合材料の創製と その特性解析に関する研究

区 分:甲

論文内容の要旨

Particle release and surface damage depend on environmental and mechanical stresses for polymer nanocomposites used in infrastructure, construction, automotive and aerospace applications. Polymer/clay nanocomposites have attracted significant attention due to the low cost of clay minerals, relatively simple preparation, and fairly predictable stiffening behavior when introduced into polymer matrix. Halloysite nanotubes (HNTs) have a unique nanotubular structure that, in addition to reinforcement and thermal stability, may provide additional functional properties for composite application. This thesis is concerned with the selective modification of the inner and outer surfaces of HNTs, the use of modified HNTs as nanocontainers for phosphorus compounds, and the investigation of structure-property relationship for sustainable polymer nanocomposites based on surface modified halloysite nanotubes.

In Chapter 1, background on the applications of phosphorus-based flame retardants, the unique structure and application of HNTs, and prior structure-property relationships for polymer/inorganic nanocomposites are introduced.

Chapter 2 is concerned with the chemistry of HNTs and selective modification of inner and outer surfaces using different modifiers, such as aminosilane groups. *N*-(2-aminoethyl)-3-aminopropyltri-methoxysilane (AEAPS) and *n*-octadecyltrimethoxysilane (OTMS) organosilane agents were selected to modify halloysite surface through a chemical vapor adsorption (CVA) process. The results show both AEAPS and OTMS are immobilized on the surface of the HNTs. The OTMS modifier has long alkyl tails and shows stronger affinity with the polymer matrix than the AEAPS modifier, which has shorter alkyl tails and amino functionalities. The use of different modifiers allows study of the modification effect using different treatments on the performance of the nanocomposites.

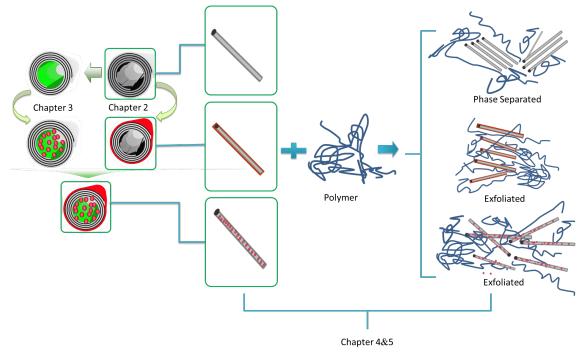
In Chapter 3, the selective modification of the inner surface of tubular halloysite with octadecylphosphonic acid (ODP) is studied. The inner-modified HNTs are used as inorganic nanocontainers for organic anti-flammable molecules, which were prepared by a pulling and breaking vacuum method. The efficiency of loading and release of the hydrophobic flame retardant, bisphenol-A bis(diphenyl phosphate) (BDP), was evaluated by nitrogen adsorption-desorption, and UV-visible spectroscopy. The results show that the inner lumen of ODP modified halloysite is loaded with hydrophobic BDP and that the flame retardant is released from the clay nanotubes linearly over 60 hours.

In Chapter 4, the modified HNTs were introduced to polycarbonate (PC) matrix. The PC/HNT nanocomposites were prepared by a combination of solution mixing, precipitating, and compression molding. The dispersion state of modified HNTs in PC was observed by optical microscopy, scaning electron microscopy (SEM), and transmission electron microscopy. The storage modulus (E') and thermal

stability of the PC nanocomposites are enhanced by introduction of the modified HNTs. OTMS-modified HNTs/PC nanocomposites showed higher performance than the AEAPS-modified HNTs/PC nanocomposites, which was attributed to the stronger interaction between the PC matrix and the hydrophobic alkyl groups of OTMS. The results show that a very low amount of modified HNTs can be used to substantially improve thermal stability of PC.

In Chapter 5, the mechanical and thermal properties of polyurethane (PU) nanocomposites reinforced with modified HNTs investigated. The nanocomposites were prepared using a solution-casting process. Anti-flammable agent-loaded HNTs/PU nanocomposites were prepared in advance by a bar-coating process. The dispersion state and reinforcing effect of the modified HNTs on the PU nanocomposites were investigated by SEM, tensile test, and dynamic mechanical analysis. The results show that a low concentration of modified HNTs remarkably improves mechanical properties of PU nanocomposites. The application of modified HNTs for flame retardant applications was also demonstrated by loading hydrophobic bisphenol-A bis(diphenyl phosphate) (BDP) into the inner lumen of HNTs. To compatibilize the hydrophilic lumen with the hydrophobic flame retardant, the HNTs were initially treated with octadecylphosphonic acid (ODP). The exterior surface was subsequently modified with AEAPS using a CVA process. The AEAPS-modified HNTs containing BDP show improved flame retardant performance without sacrificing mechanical properties.

In Chapter 6, conclusions and future directions are provided. This work demonstrates that anti-flammable molecules may be loaded into the hydrophobic lumen of HNTs and released to improve thermal stability. The surface modified HNTs containing phosphonic anti-flammable agent with polymer matrix show the thermal stability enhancement due to the release of BDP on the heating, without sacrificing mechanical properties. The findings have potential utility for smart flame retardant composite systems, and are anticipated to broaden the practical use and applications of halloysite nanotubes-based polymer nanocomposite materials.



Scheme 1. Schematic Representation of This Thesis.