Available online at www.sciencedirect.com
ScienceDirect
Current Opinion in Solid State and Materials Science 10 (2006) 73–80
Current Opinion in Solid State & Materials Science

Physical properties of polymer/clay nanocomposites

Clois E. Powell, Gary W. Beall *

Center for Nanophase Research, Texas State University, San Marcos, TX 78666, United States

Received 20 September 2006; accepted 21 September 2006

Abstract

Interest in polymer/clay nanocomposites began in 1989 with the publication of a paper by the Toyota Central Research group detailing very unusual physical property improvements in a nylon 6/clay nanocomposite. This sparked a very large worldwide effort of research on these type of composites. This paper looks at the state of knowledge about polymer/clay nanocomposites and the general trends seen in selected physical properties and the theoretical basis if know for the observed changes. The paper is not meant to be an exhaustive review of the thousands of papers currently published on the subject. Particular emphasis is given to the ability of modified Halpin–Tsai and Mori–Tanaka re-enforcement theories to predict the modulus of a true exfoliated nanocomposite. Data indicates that the level of exfoliation in these composites is one of the critical parameters in determining changes in properties. In addition to physical properties such as modulus and impact strength other phenomena such as improved flame retardancy and gas barrier properties are discussed.

Keywords: Nanocomposites; Engineering properties; Flame retardancy; Gas barrier properties; Halpin–Tsai

1. Introduction

Polymer/clay nanocomposites have a long history of development. The progress of development has been reported since the nineteen sixties and early seventies [1–4]. The field flourished after workers at the Toyota Central Research Laboratories reported a nylon 6/clay nanocomposite that was utilized in a timing belt cover on the Toyota Camry [5–9]. This revelation prompted an expansion of activity with a wide range of polymer types. The nylon 6/clay nanocomposites exhibited substantial enhancements of the physical properties of the composite relative to the pure nylon 6 polymer. These physical property improvements include increases in tensile strength, modulus, and heat distortion temperature without loss of impact strength. The maintenance of the impact strength in these composites with substantial increases in strength and stiffness was surprising. The decrease of water uptake and gas barrier improvements of the nanocomposites were substantially improved when compared to pure nylon. This series of papers initiated a huge research effort throughout the world on polymer/clay nanocomposites.

The ultimate clay nanocomposite is formed when individual clay plates are completely dispersed into a polymer matrix. This is referred to as full exfoliation. This type of composite yields the maximum improvement in properties because maximum reinforcement is achieved. In many cases the composites reported in the literature are intercalated or partially exfoliated. Intercalated systems are characterized by insertion of polymer between plates of clay with retention of well defined spacing distance between the plates. This spacing is called the gallery spacing. The spacing can be measured by wide angle X-ray diffraction. The X-ray diffraction pattern in many cases can be misleading in determining the level of intercalation/exfoliation. Disordered systems with a distribution of spacings mimic the pattern of an exfoliated system. The only reliable technique for establishing the extent of exfoliation in nanocomposites is transmission electron microscopy.

The clays utilized in these composites belong to the smectite family. These clay are characterized by a 2:1

* Corresponding author. Tel.: +1 512 245 8796; fax: +1 512 245 2374.
E-mail address: gb11@txstate.edu (G.W. Beall).

1359-0286/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cossms.2006.09.001

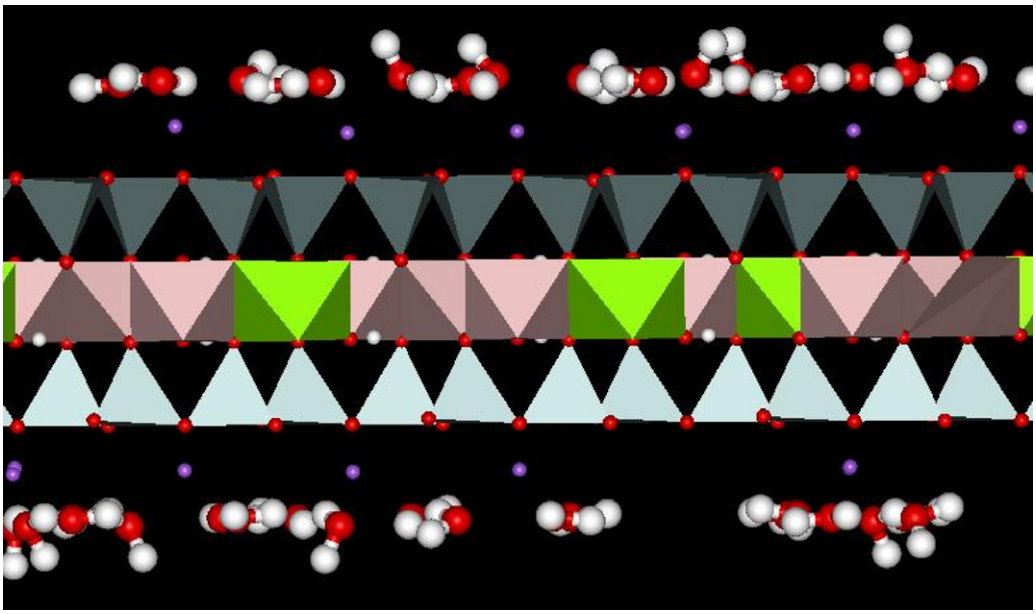

Fig. 1. Representation of the two to one structure of montmorillonite showing the central octahedrally coordinated Aluminums sandwiched between two tetrahedrally coordinated silicons. Atoms above and below the layer are exchangeable cations and their associated waters of hydration.

structure built of a central layer of octahedrally coordinated metal, normally Al^{3+} or Mg^{2+}, sandwiched between two tetrahedral coordinated layers of silicon. Fig. 1 is a model of this structure viewed from the edge of the plate. The morphology of these platy materials is characterized by a thickness of one nanometer. The two other dimensions are in the range of 100–1500 nanometers. The surface area of individual plates is greater than 750 m^2/g. This large surface area and aspect ratio dominate the interaction of these materials with polymers. Clays require surface modification for compatibility with a polymer of interest.

Isomorphous substitution in the crystal structure of these clays is common. In montmorillonite, the most common commercial nanoclay, the octahedral metal layer contains Al^{3+} which is replaced by Mg^{2+} or Fe^{2+}. Isomorphous substitution results in a charge imbalance in the structure. This is compensated by exchangeable cations on the surface of the clay plate. The exchangeable cation is normally sodium, potassium, calcium, or magnesium. The clay is normally very hydrophilic and will disperse into aqueous solutions forming thixotropic gels. This hydrophilic character makes them suitable for polymer systems that are water soluble or dispersable such as polyvinylalcohol, polyethylene oxides, latex, and polyvinylpyrrolidone. In order to render these clays compatible with hydrophobic polymers, ion exchange reactions utilizing organic onium ions are employed. The most common onium ions are quaternary ammonium ions. Most of these materials are derived from natural fats and oils making them hydrophobic. The surface of the clay can also be modified with organic molecules that contain appreciable dipole moments. These molecules do not ion exchange but form ion-dipole bonds to the exchangeable cation on the surface.

In most commercially available clay the average exchange capacity is in the range of 95 meq./100 g of clay. When this type of clay is exchanged fully with quaternary ammonium ions there is an appreciable amount of clay silicate surface still available for interaction with polymers. Small amounts of selected polymers can be mixed with the quaternary amine prior to treating the clay. The resulting surface modified clay will be more hydrophobic. The polymer apparently covers the silicate surface where exchange sites do not exist.

A fourth type of treatment is edge treatment of the clay with coupling agents. The edges of the clay plates are terminated with metal and silica hydroxides. These hydroxides can act as a barrier to hydrophobic polymer entering the clay gallery for exfoliation. Silane coupling agents can react with these hydroxides via condensation reactions. Silane coupling agents are available with a variety of functional organic groups. This allows the edges of the plates to be tailored to the polymer of interest. The edge treatment appears to effect the kinetics of intercalation but not the ultimate formation of and characteristics of the final nanocomposite.

The use of surface modified clays to form polymer nanocomposites in a large variety of polymers has been thoroughly reviewed recently by Ray et al. [10]. In this paper we will not attempt to cover in detail all of these nanocomposites. This review will describe the general physical properties observed for nanocomposites and the predictions that can be made about their properties. The method of formation of these composites will not be covered in detail. The majority of the examples fall into two categories concerning the method of formation. The methods are in situ polymerization and melt compounding. In in situ polymerization, the polymer is being produced in the presence of