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Evaluation of Intercalation and Exfoliation behaviour in Polymer based Clay Nanocomposites

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Abstract

Intercalation and exfoliation phenomena have investigated in the polymer composite that reinforced with clay nanoparticle, so on expressed as nanocomposite materials. When such organoclays are dispersed in a polymer or a polymer precursor, further intercalation can occur and in ideal considerations will lead to complete separation of the layers or exfoliation. Since the improvements in properties of polymer nanocomposites are directly related to the quality of clay intercalation and exfoliation, it is important to study the intercalation and exfoliation. The result of these phenomena is too efficient reinforcing effect because the layers are highly anisometric (1 nm thick and hundreds of nm in diameter) and a relatively small amount of clay can give rise to a very large number of particles with a correspondingly large surface area. To characterization of these phenomena the two techniques, X-ray diffraction (XRD) and transmission electron microscopy (TEM) are commonly used that both provide useful information.

Review Article

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INTRODUCTION

Polymer nanocomposites based on layered silicate reinforcement materials continue to attract significant attention. These reinforcements, which may be naturally occurring or synthetic, possess a structure consisting of negatively charged aluminosilicate layers less than 1 nm thick, closely associated in stacks, with counterbalancing cations like sodium along with loosely bound water molecules located in the space between the layers. By appropriate treatment, the metal cations can be replaced by larger organic ions (intercalants) that increase somewhat the interlayer distance[1]. Basically, polymer–clay composites are divided into three general types: phase-separated, conventional micro composites, intercalated nanocomposites (in which polymer molecules intercalate into clay galleries), and exfoliated nanocomposites, in which clay particles are separated into individual layers and dispersed evenly in the polymer matrix [2]. The latter two phenomena are the main interest in this article and they are considered as nanocomposites. Much attention has been concentrated on the realization and control of the exfoliation of clay layers [3]. The exfoliation behavior and mechanism are still not very clear [4].

Intercalation and Exfoliation

Polymer nanocomposites based on clay are two-phase materials in which clay particles are dispersed towards the nanometer (nm) range in the polymer matrix[5].Some of the researchers have also investigated the thermophysical and thermomechanical properties of epoxy/clay nanocomposites prepared by the sonication technique as one of the major techniques to achieve intercalation and exfoliation of clay nanoplatelets in the epoxy matrix [6]. Using this technique, the organoclay is mixed with solvent and either main component of epoxy or hardener. The sonicating organically modified clay

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nanoplatelets in solvent allows the separation of individual clay nanoplatelets. Afterward, the solvent is evaporated and removed at high temperature under vacuum. This results in intercalated/exfoliated clay/epoxy nanocomposites. It was shown that the storage modulus as well as the Tg were increased with exfoliated/intercalated clay/epoxy nanoplatelets[7]. The intercalation reinforcing effect for the storage modulus was discussed with the aid of the "pseudo-inclusion" model [8]and Tandon-Weng equations [9]. On the basis of the pseudo-inclusion model, an explanation was proposed that the larger basal spacing of expanded/intercalated clay nanoplatelets provides greater elastic modulus of nanocomposites. Some investigations are showed, in terms of intercalation and degree of exfoliation achievable by melt-state mixing processes [5]. A step forward basing has been made on the frequency shifts induced by the intercalation and exfoliation of the clays [10]. It has beeen showed that the exfoliation results in a shift of the Si–O out of plane band to higher wavenumber. Intercalation and exfoliation behavior of clay layers in the polymer matrix has characterized by a combination of WAXD and rheological methods[11].For example Graphite is a layered material made up of sheets of carbon that are one atom thick. By separating the graphite layers through intercalation and exfoliation, thin nanoplates can be formed that possess a high surface area and satisfy the high aspect ratio criterion needed for high strength composites[12]. The well-defined diffraction spots confirm the crystalline structure of the Aniline-intercalated graphite nanoplatelets (AGNPs). The combination of intercalated and exfoliated graphitic structures has been clearly revealed in these (Fig1).

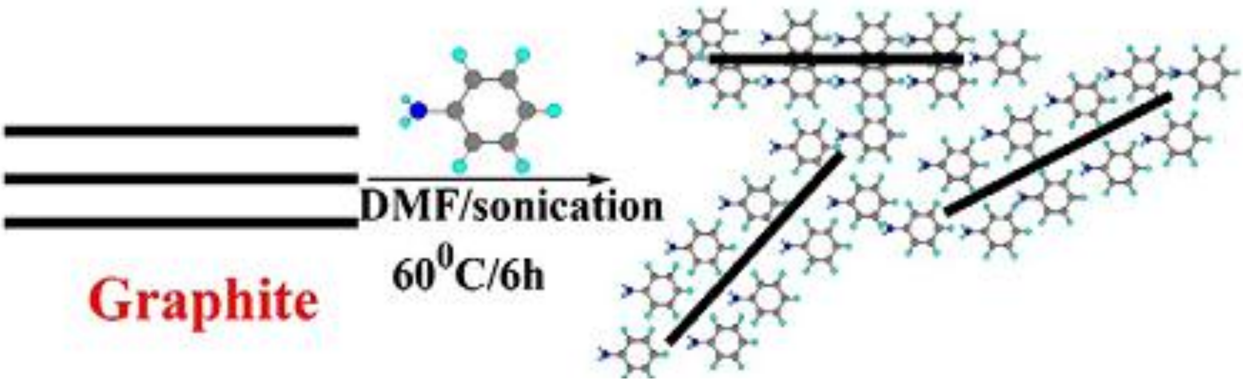

Figure1. Scheme 1shows the synthesis of the AGNPs. During the synthesis, the aniline moieties were intercalated into the graphite to form aniline-intercalated graphite [12].

In some research that have been suggested that intercalation of the polymer in the organoclay galleries is the first step leading to exfoliation of the platelets in the polymer melt [13].

Organoclay surfactants were chosen to demonstrate the effect on intercalation of varying the ammonium ion head group structure including the number of tails, tail group length, and exchange ratio [14].

Methods of Intercalation and Exfoliation

In situ polymerization is one of the methods to prepare exfoliated and intercalated polymer/clay nanocomposites. Generally, in situ polymerization includes two stages: the first is to mix the polymer precursor or monomer and clay; the second is in situ polymerization in the presence of clay. It is suggested that the in situ polymerization is responsible for the exfoliation of clay layers in the polymer matrix [11].

Exfoliation of clay layers is attributed to the formation of cross linked structures inside the clay galleries during the curing process. The realization of exfoliation during the first mixing stage has more advantages compared with the situation when exfoliation occurs during the step [15]. This gives better control on the degree of exfoliation, and it is also easier to evaluate whether the material is exfoliated before the formation of the products[16].The term intercalation, which refers to incorporation of molecules other than the surfactant into the gallery, e.g. liquid monomer, is also widely used in connection with polymer melt/clay composites[17].

Monitoring of Intercalation and Exfoliation

The scientific and interest for polymer aluminium silicate clay nanocomposites has risen dramatically over the last decades, whereas the monitoring of the extent of intercalation and exfoliation using an efficient, fast and convenient method remains an important issue. Infrared spectroscopy constitutes a very promising characterization technique to fulfill this role [18].

Transmission electron microscopy (TEM) and X-ray diffraction (XRD) are useful techniques to monitor and observe the change of the basal spacing of intercalated clay nanoplatelets[19].The XRD patterns indicate a good interaction between organoclay and the polymer matrix, which helps expand clay interlayer spacing as well as the dispersion of clay particles[20]. Other researchers have made similar findings in different material systems [21, 22].

CONCLUSION

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In this article the intercalation and exfoliation processes was reviewed. It was shown that the storage modulus as well as the glass transition thermal (Tg) of polymers were increased with exfoliated/intercalated clay/epoxy nanoplatelets in the structure of these materials. By separating the layer of nano fillers in the process of intercalation and exfoliation, thin nanoplates can be formed that possess a high surface area and satisfy the high aspect ratio and by increasing of this parameter, improve in the mechanical and thermal properties of manufactured nanocomposites were resulted. On the other hand intercalation and exfoliation of clay nanofiller in the structure of polymer enhance the thermal and electrical conductivity of these materials.

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