

Montmorillonite polyaniline nanocomposites: Preparation, characterization and investigation of mechanical properties

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ABSTRACT

The interest in clay polymer nanocomposites (CPN) materials, initially developed by researchers at Toyota, has grown dramatically over the last decade. They have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials' properties when compared with virgin polymer or conventional micro- and macro-composites. These improvements can include high moduli, increased strength and heat resistance, decreased gas permeability and flammability, optical transparency and increased biodegradability of biodegradable polymers. Such enhancement in the properties of nanocomposites occurs mostly due to their unique phase morphology and improved interfacial properties. Because of these enhanced properties they find applications in the fields of electronics, automobile industry, packaging, and construction. This study aims at investigating the mechanical property enhancement of polyaniline (PANI) intercalated with montmorillonite (MMT) clay. The MMT–PANI nanocomposites displayed improved mechanical properties compared to the neat polymer or clay. The enhancement was achieved at low clay content probably due to its exfoliated structure. The increased interfacial areas and improved bond characteristics may attribute to the mechanical property enhancement.

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1. Introduction

Nanocomposites are a promising new class of technologically advanced materials, consisting of two or more phases in which at least one of its phases has one or more dimensions (length, width or thickness) in the nanometer size range, usually defined as 1–100 nm. Nanocomposites show conspicuously enhanced mechanical, thermal, optical and electro chemical properties compared to their neat or conventional composites [1]. The commonly used layered silicates for the preparation of clay–polymer nanocomposites (CPN) belong to the same general family of 2:1 layered or phyllosilicates. Montmorillonite (MMT), hectorite, and saponite are the most commonly used layered silicates. Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. Stacking of the layers leads to a regular van der Waals gaps between the layers, which are called

the *interlayer* or *gallery* regions. Isomorphic substitution within the layers (for example, Al³⁺ replaced by Mg²⁺ or Fe²⁺ or Mg²⁺ replaced by Li⁺) generates negative charges in the layers that are counter-balanced by alkali and alkaline earth cations situated inside the galleries. This type of layered silicate is characterized by a moderate surface charge known as the cation exchange capacity (CEC), and is generally expressed as mequiv./100 g [1–3].

Three main types of clay polymer nanocomposites can be obtained when a layered silicate is dispersed in a polymer matrix: conventional or phase separated composite, intercalated nanocomposite and exfoliated nanocomposite. If the polymer is not intercalated between the silicate sheets and the clay particles are just dispersed within the polymer matrix the product obtained is a microcomposite. The phase separated composite has the same properties as traditional microcomposites. Intercalated structures are formed when a single (or sometimes more) extended polymer chain is intercalated (sandwiched) between the silicate layers. The result is a well-ordered multilayer structure of alternating polymeric and inorganic layers. Exfoliated or delaminated structures are obtained, when the silicate layers are completely separated from the clay particles and are uniformly dispersed in the continuous polymer matrix. The exfoliation configuration is of particular interest because of its maximized polymer–clay interactions making the entire surface of the layers available for the polymer. This should

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lead to the most significant changes in mechanical and physical properties [1–4]. Excellent reviews of over 100 journal page length on the preparation, characterization, processing and applications of polymer/clay nanocomposites are already in the literature to demonstrate the importance and usefulness of these novel materials. Applications are envisioned in antistatic surface coatings, corrosion protection, electromagnetic shielding, electrochromism, photovoltaics, organic electrodes, electrochemical capacitors, sensors, batteries and accumulators [1–4].

Polyaniline (PANI) is well-known for its conducting ability. They have versatile promising applications in the field of energy storage, electronic and optical devices, sensors and much more. While conducting polymers such as polyaniline and polypyrrole exhibit excellent electrical conductivities and outstanding thermal stability, their mechanical properties are poor leading to a reduced processability [5].

In this work, a host of conducting polymer PANI has been combined with a smectite type clay montmorillonite (Bentonite) (MMT) in an aqueous medium to produce MMT–PANI nanocomposites which have the conducting properties of the conducting polymer and some mechanical properties of the insulating clay. Various compositions with different clay contents were prepared with a constant polymer concentration and their structures were characterized and their mechanical properties were investigated. MMT–PANI and PPY–MMT (PPY = polypyrrole) nanocomposites are not new and the vast literature is already available to account for their preparation, characterization and electrical properties of these interesting materials. The authors have already contributed significantly on the novel methods of MMT–PANI synthesis, their characterization and the investigation of their electrical properties [6–13]. A few articles also appear in the literature on the mechanical properties of MMT–PANI nanocomposites [14–16]. However, most of these studies have concentrated on intercalated MMT–PANI nanocomposites. In this paper, we show that by varying the composition of parent materials in the preparation of MMT–PANI nanocomposites, the optimum composition corresponding to best mechanical properties could be investigated and that the nanocomposite is then present in the exfoliated structure where MMT platelets have been separated out from the clay particles and dispersed in the PANI matrix. This optimum composition is 23% clay in PANI at which the two species are at their maximum interactions leading to a very stable structure.

2. Experimental

2.1. Materials

The starting material used for the experimental work was a natural raw material of Bentonite clay purchased from India. The Bentonite clay is a component of sodium montmorillonite (Na^+ -MMT), which has a cation exchange capacity (CEC) of 100 milliequivalents (mequiv.) per 100 g, has high aspect ratio and can swell 14–16 times upon hydration [17]. Bentonite which is pale yellow in colour has a

molar mass of $540.46 \text{ g mol}^{-1}$ and has a density of 2.35 g ml^{-1} . Aniline (colourless when distilled) and all other chemicals used in the preparation of montmorillonite polyaniline (MMT–PANI) nanocomposite were purchased from Aldrich and used as received except for aniline which was double distilled and stored at 4°C . It has a molar mass of 93.13 g mol^{-1} and a density of 1.022 g ml^{-1} (at 25°C).

2.2. Preparation

The MMT–PANI nanocomposites were prepared by *in situ* intercalative polymerization method. An amount of 5 g of dry MMT (Bentonite) was dispersed in 100 cm^3 of 1 mol dm^{-3} HCl and stirred for 24 h by using a magnetic stirrer. The suspension was centrifuged and the supernatant discarded. This procedure was repeated until the supernatant is free of chloride ions (tested using an AgNO_3 solution) and the slurry was dried at 120°C for 2 h. This ensures the complete exchange of cations present in the clay for H^+ ions yielding the H^+ -MMT. The H^+ of H^+ -MMT were exchanged for anilinium ions by the routine procedure of ion exchange using 100 cm^3 of 1 mol dm^{-3} anilinium chloride solution. The anilinium ion exchanged MMT was then subjected to thorough and repeated washing with distilled water until the supernatant was free of chloride ions. The residue was then treated with acidified $0.4 \text{ M } (\text{NH}_4)_2\text{S}_2\text{O}_8$ while stirring vigorously for 24 h in order to polymerize the anilinium ions present within the intergalleries. This has resulted in green coloured polyaniline form known as the emeraldine salt (EMS) containing MMT nanocomposite (EMS–MMT). The samples were then thoroughly washed by the repeated dispersion in distilled water followed by centrifuging and decanting the supernatant until the supernatant is free of chloride ions. The resultant slurry was dried under room temperature for 3–4 days.

Various compositions with different clay contents (2, 3, 4, 5, and 10 g) were prepared with constant polymer content and the resulted samples were named as EMS–MMT2, EMS–MMT3, EMS–MMT4, EMS–MMT5 and EMS–MMT10, respectively. Rectangular bars with dimension ($40 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$) were pressed uniaxially at 4 MPa for making the test samples and were vacuum dried at ambient temperature for 2 h prior to the testing.

2.3. Characterization

X-ray diffraction (XRD) spectra (Seimens D-5000, Radiation Cu $K\alpha$ $\lambda = 0.1540562 \text{ nm}$) were recorded for raw MMT, H^+ treated MMT and EMS–MMT series of compositions at various temperatures. Samples were prepared by making thin films of the composition on glass plates using distilled water for taking the XRD spectra. The XRD spectra were taken at (i) ambient laboratory temperature and (ii) immediately after the heat treatment at 150°C for 2 h.

2.4. Testing of properties

Mechanical properties of the materials such as flexural strength also known as modulus of rupture (MOR), Young's modulus (Y), fracture toughness (K_{Ic}), hardness and impact strength were investigated [18]. Most of the mechanical properties (MOR, Y and K_{Ic}) were explored using a locally made universal mechanical testing machine, hardness was determined by an FM-7 digital micro-hardness tester and the impact strength was measured using an impact testing machine which was locally made.

The flexural strength is defined as the maximum stress a material can bear before failure and is often referred to as the modulus of rupture (MOR) or the bend strength. Experimentally the MOR for a rectangular bar can be determined either by 3-point bending or by 4-point bending. In the case of 4-point bending (Fig. 1), which was the configuration used for the MMT–PANI nanocomposites, the MOR can be calculated according to the following equation:

$$\text{MOR}_{(4\text{-point})} = \frac{3(L-a)P}{2bh^2} \quad (1)$$

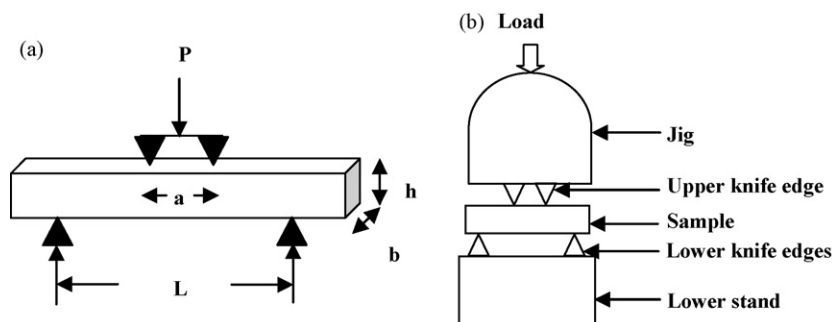


Fig. 1. The 4-point bending configuration: (a) the sample; (b) the whole setup.

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