

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

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## ARTICLE INFO

### Article history:

Received 11 June 2008

Received in revised form 14 August 2008

Accepted 16 August 2008

### Keywords:

MMT–PANI nanocomposites

MOR

Young's modulus

Fracture toughness

## 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. Isomorphous substitution within the layers (for example, Al<sup>3+</sup> replaced by Mg<sup>2+</sup> or Fe<sup>2+</sup> or Mg<sup>2+</sup> replaced by Li<sup>+</sup>) generates negative charges in the layers that are counterbalanced 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 ( $\text{Na}^+$ -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  $2.35 \text{ g ml}^{-1}$ . 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  $4^\circ\text{C}$ . It has a molar mass of  $93.13 \text{ g mol}^{-1}$  and a density of  $1.022 \text{ g ml}^{-1}$  (at  $25^\circ\text{C}$ ).

### 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  $100 \text{ cm}^3$  of  $1 \text{ mol dm}^{-3}$  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  $\text{AgNO}_3$  solution) and the slurry was dried at  $120^\circ\text{C}$  for 2 h. This ensures the complete exchange of cations present in the clay for  $\text{H}^+$  ions yielding the  $\text{H}^+$ -MMT. The  $\text{H}^+$  of  $\text{H}^+$ -MMT were exchanged for anilinium ions by the routine procedure of ion exchange using  $100 \text{ cm}^3$  of  $1 \text{ mol dm}^{-3}$  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,  $\text{H}^+$  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  $150^\circ\text{C}$  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:

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

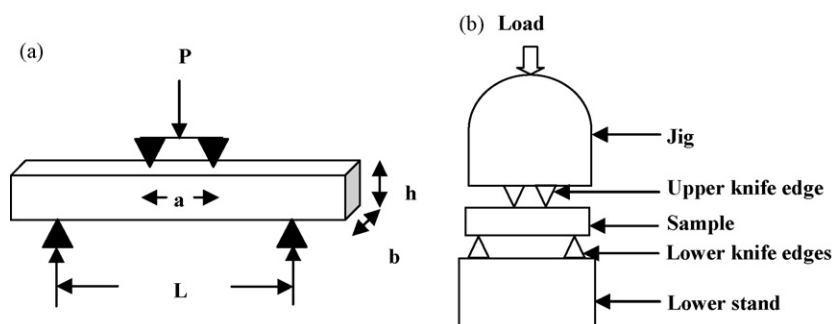


Fig. 1. The 4-point bending configuration: (a) the sample; (b) the whole setup.

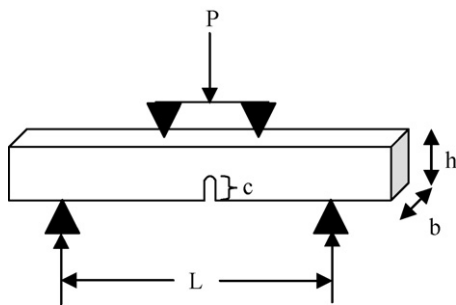


Fig. 2. Single edge notch beam configuration.

where MOR is the modulus of rupture measured in Pascal and  $L$ ,  $a$ ,  $P$ ,  $b$  and  $h$  stand for the distance between lower knife edges, the distance between upper knife edges, the maximum applied load, width of the sample and height of the sample, respectively.

Young's modulus ( $Y$ ) (also known as tensile modulus) is a measure of the stiffness of a given material. This can be experimentally determined from the slope of a stress–strain curve created during tensile tests conducted on a sample of the material. Young's modulus,  $Y$ , can be calculated by dividing the tensile stress by the tensile strain (Eq. (2)):

$$Y = \frac{\text{tensile stress } (\sigma)}{\text{tensile strain } (\varepsilon)} = \frac{3(L-a)P/2bh^2}{6hy/(1-a)(1+2a)} \quad (2)$$

where  $y$  stands for the depression at the load point. For the MMT–PANI nanocomposite the Young's modulus was determined using the universal mechanical testing machine with 4-point bending at a cross head speed of  $9.4 \times 10^{-3} \text{ mm s}^{-1}$ .

Uniaxially pressed rectangular samples were prepared by introducing a notch ( $<1/3$  of the height of the sample) as shown in Fig. 2 to find the fracture toughness using the universal mechanical testing machine at a speed of  $9.4 \times 10^{-3} \text{ mm s}^{-1}$ . For the 4-point bending fracture, the Eq. (3) was used to calculate the fracture toughness:

$$K_{Ic} = \frac{3Pd}{bh^2} c^{1/2} \left[ 3.86 - 6.15 \left( \frac{c}{h} \right) + 21.7 \left( \frac{c}{h} \right)^2 \right]^{1/2}; \quad d = \frac{L-a}{2} \quad (3)$$

where  $c$  stands for the length of the notch.

Hardness of the samples was measured by using an FM-7 digital micro-hardness tester with a square based pyramidal diamond indenter which has a phase angle of  $136^\circ$ . Specimens were made from the MMT–PANI nanocomposites by pressing pellets of 1 cm diameter at a pressure of 15 kPa. The specimen was placed on the elevation stage and allowed the indenter to move down and stay on the specimen surface for a dwell time of 10 s and then moved up to the starting position to release the load (1 kgf). The indentation was then focused and the diagonal lengths were read. HV was finally determined by the following formula:

$$HV = \frac{F}{S} = \frac{2F \sin \theta/2}{d^2} = 1.854 \frac{F}{d^2} \quad (4)$$

where HV is the Vickers hardness number measured in  $\text{kg f mm}^{-2}$ ,  $F$  is the test load in kgf,  $S$  is the surface area of the indentation,  $d$  is the average diagonal length of the indenter and  $\theta$  is the face angle of the pyramidal diamond indenter.

A homemade impact tester, designed according to the drop weight technique, was used to find the impact strength of the MMT–PANI nanocomposite. Uniaxially pressed rectangular bars from the MMT–PANI nanocomposite were used to find the impact strength. The striker was released from an appropriate height and allowed to strike the specimen which was rest on supports against two anvils. Upon impact, the specimen is in 3-point bending, which results in the initiation and propagation of a crack from the root (bottom) of the notch. After breaking the specimen, the striker was raised to a height ( $h$ ). The energy absorbed in breaking the specimen can be calculated as the difference in potential energy before release of the striker and the potential energy at the instant of zero velocity after specimen impact and is given in the following equation:

$$\text{I.E.} = mgh \frac{H_m - H}{H_m - H_i} \quad (5)$$

where I.E. is the impact energy of the sample measured in J,  $m$  is the total mass of the crosshead,  $g$  is the gravitational acceleration,  $h$  is the drop height,  $H_i$  is the initial reading of the scale,  $H_m$  is the maximum reading of the scale without the sample and  $H$  is the final reading of the scale with the sample.

## 3. Results and discussion

### 3.1. Characterization

#### 3.1.1. Natural montmorillonite

The XRD spectra of the natural MMT kept in the ambient laboratory temperature and immediately after the heat treatment at  $150^\circ\text{C}$  for 2 h are shown in Fig. 3. The Bragg diffraction peak indicates the (001) layer spacing ( $d$ -spacing) of MMT. The layers of MMT are stacked along a line perpendicular to (001) basal plane. The  $d$ -spacing of MMT at  $25^\circ\text{C}$  is 15.43 and 9.96 Å. The MMT clay layers are negatively charged by the isomorphous substitutions raised by the positive cations residing in the interlayer spacing so that the natural MMT can easily absorb water through covalent hydrogen bonds and can swell due to the layers of water molecules present within the interlayer space. These interlayer water molecules are loosely bound by weak van der Waals forces so that they can be easily removed at higher temperature. When the same sample was oven dried at  $150^\circ\text{C}$  for 2 h, the (001) layer spacing reduced to 9.96 Å, which is attributed to the absence of water molecules within the MMT. The presence of one water layer increases the  $d$ -space to 12.6 Å, two water layers to 15.6 Å and three water layers to 18.6 Å and so on [10]. Hence the interlayer cations of MMT at ambient laboratory temperature have absorbed two layers of water molecules.

#### 3.1.2. The hydrogen ion treated MMT

The cations present within the interlayer spacing of the natural MMT were ion exchanged with  $\text{H}^+$  so as to facilitate the uptake of aniline. The corresponding XRD spectra shown in Fig. S1 in supplementary materials, indicate no significant changes in  $d$ -spacing with clay content and the  $d$ -spacing remains almost the same (see Table ST1 in the supplementary materials). The XRD indicates the  $\text{H}^+$  ions present within MMT are also hydrated with two water layers at room temperature. However at high temperature water got removed similar to natural MMT.

#### 3.1.3. The MMT–PANI nanocomposite

The XRD spectra of the MMT–PANI (EMS–MMT series) nanocomposites (Supplementary Materials Fig. S2) indicate that at room temperature the  $d$ -spacing (Supplementary Table ST2) of the natural MMT is greater than that of the EMS–MMT series. This is due to the excessive hydration of simple inorganic cations in natural

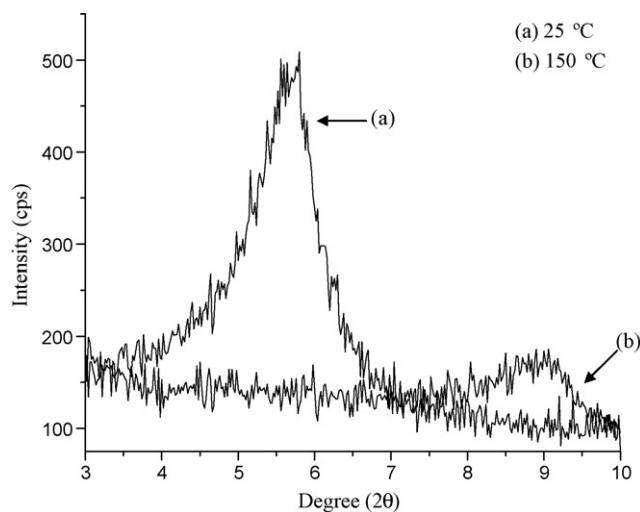


Fig. 3. XRD spectra of the natural MMT at (a) ambient laboratory conditions and (b) after heat treated for 2 h at  $150^\circ\text{C}$ .

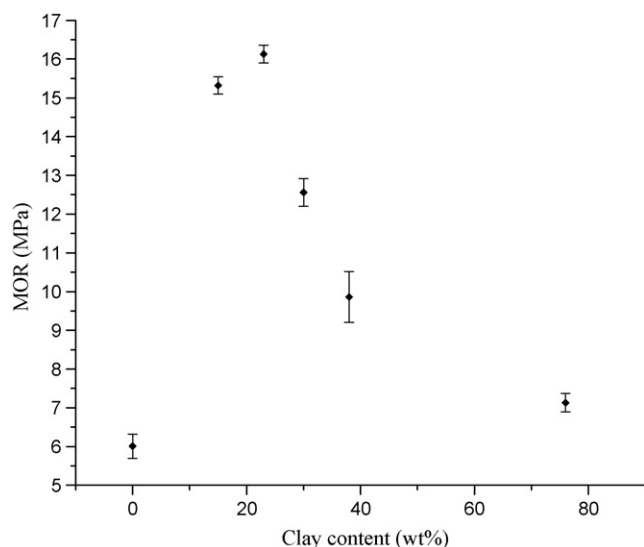


Fig. 4. The modulus of rupture (MOR) of the EMS–MMT series for various clay contents (average values of five repeated readings).

MMT and the lesser degree of hydration of the hydrophobic organic cations present within the interlayer space under ambient laboratory condition. However, when the samples were heat treated at 150 °C for 2 h before the test, they became anhydrous and gave an increase in the *d*-spacing which is greater than the natural MMT. Hence it is evident that the intercalated organic polymer gives rise to the *d*-spacing in the EMS–MMT nanocomposite.

There are two compositions (EMS–MMT2 and EMS–MMT3) which contain the lowest clay content remained unchanged in the XRD indicating exfoliated structure while the others have either a region of intercalated structure or a region of exfoliated structure or a region of agglomeration. In low clay content the driving force of polymerization is much higher to overcome the attractive electrostatic force between the negatively charged silicate layers and the interlayer cations that leads to exfoliation. Nanocomposites which have exfoliated structures are desirable to have attractive mechanical properties as the dispersed clay layers give reinforcement in every direction to the continuous polymer matrix leading to better mechanical properties.

### 3.2. Mechanical properties

Mechanical properties are the response of matter to applied forces. These properties are controlled largely by the inter-atomic forces or the inter-atomic potential energy. It has been well established that at least with common organic polymers such as nylon, poly(vinyl chloride) and so on, the clay–polymer nanocomposites (CPNs) show enhanced mechanical properties compared to their virgin material or their microcomposites [19,20].

#### 3.2.1. Modulus of rupture (MOR)

The MOR of the EMS–MMT series were calculated and plotted against clay contents (Fig. 4). The intercalation of the MMT clay into PANI matrix improved its bending strength (MOR) dramatically. The perfect intercalated and exfoliated structures provide more interfacial surface areas than phase separated (agglomerated) structures so that the MMT–PANI nanocomposite has higher strength when compared to the neat polymer.

The MOR mostly increased at low clay contents but decreased at higher clay contents. The increase in strength at low clay contents is mainly due to its exfoliated structure. The compositions that

have low clay contents have exfoliated structure while the others have intercalated structure (evidence from XRD). Hence the better mechanical strength at low clay contents arises from the reinforcement of the dispersive clay layers. Furthermore, the stresses are much more effectively transferred from the polymer matrix to the inorganic clay in exfoliated structure resulting in an increase in strength. The degradation of properties at higher clay contents is believed to be caused by phase-separated structures and also by defects in the structures.

#### 3.2.2. Young's modulus

Young's modulus, expressing the stiffness of the material, has shown (Fig. 5) to be strongly enhanced when nanocomposites are formed. Young's modulus increases monotonically with increasing clay content and levels off at higher clay contents. A clay loading of 23 wt.% improved the modulus from 0.51 to 3.52 GPa. This is the optimum clay loading giving the maximum Young's modulus.

The higher improvement of Young's modulus in MMT–PANI nanocomposite to the neat polymer attribute to better dispersion and intercalation/exfoliation of nanoparticles. In general, the improvement in elastic modulus is attributed to the good dispersion of nanosize clay layers and good interfacial adhesion between the layers and the polyaniline matrix so that the mobility of polymer chains is restricted under loading. The orientation of silicate layers and polymer chains with respect to the loading direction can also contribute to the reinforcement effects. However, the decreasing the elastic modulus improvement after certain higher clay content can be attributed to the inevitable occurrence of unexfoliated aggregates.

#### 3.2.3. Fracture toughness

The fracture toughness (Fig. 6) of mode I fracture in terms of stress intensity factor of MMT–PANI nanocomposite indicate significant increase for low clay contents and decrease at higher values. The fracture behavior of MMT–PANI nanocomposite is influenced mainly by two factors which are the micro-dispersed clay particles that are well known to affect fracture toughness in continuous polymers and the crystalline morphology, especially the size and the form of crystals, of semi-crystalline polymer PANI. When the sample was loaded the clay layers might be acted as stress concentrators and should promote the formation of large number of micro-cracks

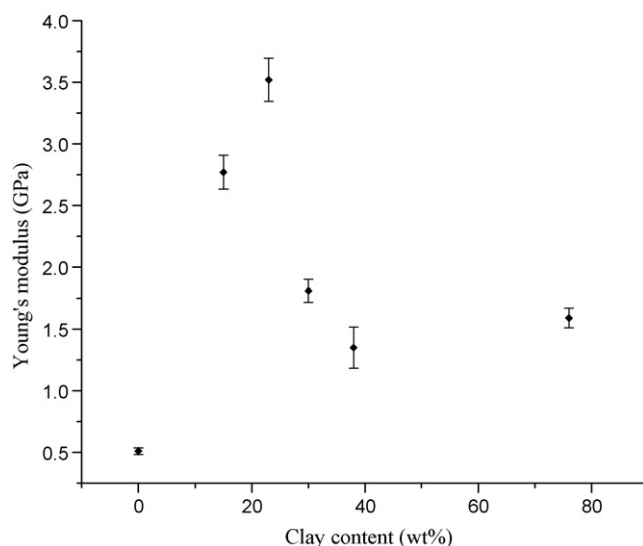
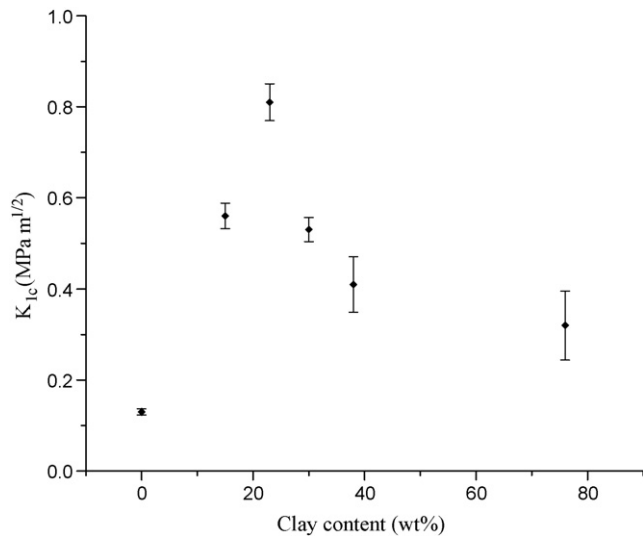


Fig. 5. The Young's modulus of the EMS–MMT series for various clay contents (average values of five repeated readings).



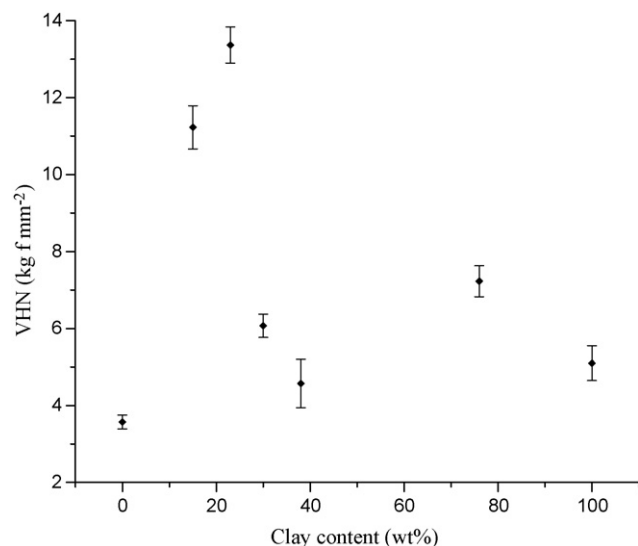
**Fig. 6.** The fracture toughness of the EMS–MMT series for various clay contents (average values of five repeated readings).

and they should increase the fracture surface by crack deflection [21]. Hence the formation of large number of micro-cracks and crack deflection are the major toughening mechanisms.

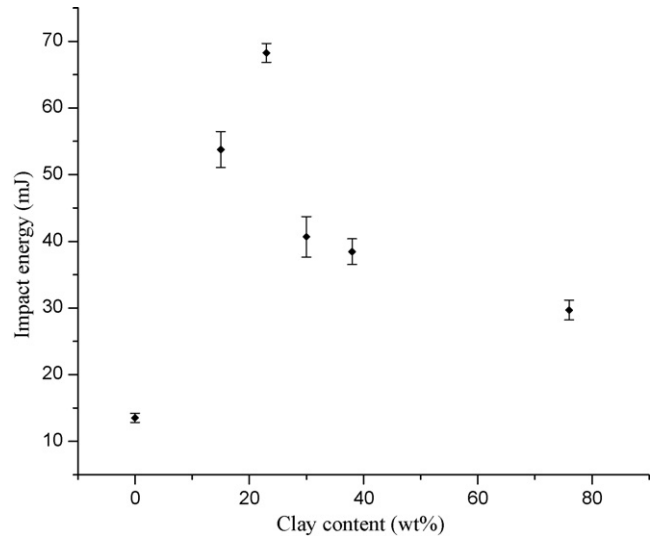
The property enhancement at low clay contents is achieved due to increased interfacial areas, improved bond characteristics and unique phase morphology of the exfoliated structure. The resistance to crack propagation which is very low at higher clay content is attributed to the larger size and lower aspect ratio of the aggregates. Thus in MMT–PANI nanocomposite the improvement of the toughness can be attributed to the breakage of the clay aggregates.

### 3.2.4. Hardness testing

The hardness of the MMT–PANI nanocomposite in terms of Vickers Hardness Number (VHN), depicted in Fig. 7 as a function of clay content increased drastically for low clay contents and decreasing for higher clay content. The bond strength and the morphology of the MMT–PANI nanocomposite play a major role in determining the hardness.



**Fig. 7.** The hardness of the EMS–MMT series for various clay contents (average values of five repeated readings).



**Fig. 8.** The impact energy of the EMS–MMT series for various clay contents (average values of five repeated readings).

The pellets prepared for the hardness testing from the MMT–PANI nanocomposite had polished surface in appearance and their magnified photograph of the indentation are shown in Supplementary material Fig. S3. The nanocomposites which have low clay content have very sharp and narrow indentation while the others have blunt and wide. The higher hardness is attributed to stronger interaction and better dispersion of the clay layers while high porosity and particle aggregation leads to poor hardness at higher clay content.

### 3.2.5. Impact testing

The impact energy of the MMT–PANI nanocomposite shown in Fig. 8 is very low when compared to other polymer systems such as nylon 6, epoxy and so on [21,22]. However, the nanocomposites have enhanced impact energy than their virgin materials.

Typically the impact strength depends on three major factors which are the bond strength, Young's modulus and surface energy. The results show higher impact energy for low clay content and it is decreasing with increasing clay amount. This is not surprising because the clay content brings brittleness to the composition and hence the low impact energy at higher clay content. The higher impact strength at low clay content is attributed to the high bond strength and Young's modulus of the exfoliated structure.

In general the impact energy of the MMT–PANI nanocomposites is much lower when compared to nylon 6 nanocomposites [23] as nylon exhibits ductility whereas MMT–PANI nanocomposites are more brittle.

## 4. Conclusion

The results indicate that the mechanical properties of the MMT–PANI nanocomposite, the MOR, Young's modulus, fracture toughness, hardness and impact energy of polyaniline significantly increased by the presence of MMT clay in the nanocomposite of PANI and MMT up to 23 wt.% of MMT and decreased at higher clay contents. The degree of exfoliation and the bond strength of the MMT clay attribute to the better mechanical properties. At higher clay content the clay aggregates present within the intercalated nanocomposites might reduce their resistance to crack propagation. So the 23 wt.% of MMT–PANI (EMS–MMT3) nanocomposite that has the optimum mechanical characteristics can be suggested for applications.

## Acknowledgements

Financial assistance by the National Science Foundation, research grant RG/2005/FR/04 and the National Research Council NRC 05–09 are gratefully acknowledged.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matchemphys.2008.08.055.

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