Research article

Properties of nanoclay PVA composites materials

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ABSTRACT

Polyvinyl alcohol (PVA)/Na-rich Montmorillonite (MMT) nanocomposites were prepared using solution method to create polymer-clay nanocomposite (PCN) material. The PCN material was studied using X-ray diffraction (XRD), demonstrating polymer-clay intercalation that has a high *d*-spacing (lower diffraction angles) in the PCN XRD pattern, compared to the pure MMT clay XRD pattern, which has a low *d*-spacing (high diffraction angles). The nano-scanning electron microscope (NSEM) was used to study the morphological image of the PVA, MMT and PCN materials. The results showed that intercalation that took place between the PVA and MMT produced the PCN material.

The mechanical properties of the pure PVA and the intercalated polymer material were studied. It was found that the small amount of MMT clay made the tensile modulus and percentage of the total elongation of the nano-composite significantly higher than the pure PVA polymer value, due to polymer-clay intercalation. The thermal stability of the intercalated polymer has been studied using thermal analytical techniques such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results showed that the PCN material is more thermally stable than the pure PVA polymer.

Keywords: Polyvinyl alcohol (PVA), Na-rich Montmorillonite (MMT), X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC), Mechanical properties

1. INTRODUCTION

Polymer-clay nanocomposite (PCN) materials have recently become a main research focus due to their unique characteristics and potential commercial applications, receiving research interest and attention from both academia and industry.[1] The addition of clay to polymers improves their properties and may result in beneficial features to the materials produced.[2] PCN materials are reported to have enhanced thermal,[3] mechanical,[4] molecular barriers,[5] flame retardation,[6] corrosion protection properties,[7−9] and electrical characteristics.[10]

The first PVA/MMT nanocomposite materials fabrication using a solvent casting method was reported by Greenland in 1963.[11] In 1997, Ogata and coworkers applied the same technique for the production of PVA/MMT composites.[12] Furthermore, in 2000, Strawhecker and Manias have developed PVA/MMT nanocomposite films with improved properties. The obtained nanocomposite films exhibited both intercalated and exfoliated regions.[13]

Yu et al, in 2003 reported the synthesis of PVA/MMT nanocomposites based on in-situ intercalative polymerization.[14] The structural characterization of the developed materials confirmed the formation of mixed intercalated/exfoliated regions. More recently, highly ordered PVA/MMT were produced by the layer-by-layer (LBL) process.[15] The obtained nanocomposites exhibited superior mechanical properties without significant reduction in optical transparency.

The PCN material that consists of PVA and layered MMT are found to have unique characteristics and improved properties. There are several publications associated with the preparation and properties of PVA−clay nanocomposite materials prepared by solution dispersion technique.[16−18] The results showed that the incorporation of nanolayers of MMT clay in PVA matrix results in an increase in thermal decomposition temperature, glass transition temperature and mechanical strength based on TGA and DSC studies.[19]

This study investigates the effect of different loading concentrations of Swy-2 (Na-rich Montmorillonite) clay when they are effectively dispersed in organic polyvinyl alcohol matrix. The poly(vinyl alcohol)/ Swy-2 nanocomposite materials are characterized by Fourier-transformation infrared (FTIR) spectroscopy, which gives an indication about the loading concentration of clay in the PCN. The interlayer spacing of the PCN and its formation have been evaluated using wide-angle X-ray diffraction (XRD). The morphological images of the PCN materials are also studied using a nano-scanning electron microscope (NSEM). The organic/water content of the PCN has been characterized using thermogravimetric analysis (TGA). Effects of the material composition on the thermal stability and the mechanical strength of PCN materials in the form of fine powder are also studied by TGA, DSC and tensile mechanical measurements.

The mechanical properties enhancement of PCN materials depends on the intercalated structure formed.[20−23] A small amount of clay substantially improves tensile strength, tensile modulus, flexural strength and flexural modulus without loss of elongation at break.[24] The mechanical properties of PCN appear to be improved by the addition of a small amount of clay, but are decreased by larger amounts of clay.[25,26] A study using X-ray photoelectron spectroscopy on PCN material has found that the presence of the clay seems to retard the chain-stripping process of degradation and enhanced char formation.[27] Previous studies showed that additions of clay by 4.2 wt% increased the tensile strength of nylon 6 from 69 MPa to 107 MPa, and the tensile modulus was doubled. This significant improvement in mechanical properties of nylon 6−clay nanocomposite was attributed to the formation of a high interfacial surface area and ionic and/or hydrogen bonds between the organic polymer and inorganic silicate.[28,29]

2. METHODOLOGY

2.1. Source of the clay samples

Swy-2 (Na-rich Montmorillonite), Crook County, Wyoming, USA clay was obtained from the Clay Minerals Society, Purdue University. Polyvinyl alcohol (PVA) was obtained from Sigma-Aldrich, Co., USA and had M_w 13,000−23,000.(WWW.CLAYS.ORG)

2.2. Preparation method of polymer nanocomposites (PNCs) using a solution method

In the solution method, the clay (in suspension) is added to a polymer solution, followed by dispersing and heating if appropriate. This method is often used for water soluble polymers.[24]

Five grams of Swy-2 MMT clay was suspended at 50°C in 30 ml of de-ionised water. One hundred grams of polyvinyl alcohol powder was dissolved in 350 ml of de-ionised water, heated at 60°C for 10 min. The clay suspensions were added slowly, continued mixing with the dissolved polymer at 60°C for 30 minutes. The mixture was moved to clean and the mortar washed. After 4 hours the dry surface of the mixture was removed and placed into a new mortar. When all the mixture dried it became similar to solid plastic. It was cut into small pieces for cryomill grinding. The cryomill grinder was used for 10 minutes to freeze the PCN using liquid nitrogen and grinding for 10 min with frequency of 5 shakings per second.

2.3. X-ray fluorescence

The chemical composition of MMT clay was measured using Energy Dispersive X-ray Fluorescence Spectrometer (ED-XRF), Philips. The ED-XRF operational parameters are 150 kV, 3 mA, 150W. The spectrum MMT was collected.

2.4. X-ray diffraction

The X-ray spectra were collected using desktop X-ray Rigaku Miniflex II diffractometer equipped with Cu-K$_\alpha$ source ($\lambda = 1.5404$ Å), Japan. It was operated at 50 kV and 20 mA and scans were obtained in a 2θ range from 3° to 30°, with a 2° step size. The X-ray diffraction (XRD) patterns were collected using Rigaku software (version 1.2) and analyzed using Rigaku data analysis software PDXL version 2, 2010. The XRD patterns of the pure MMT and the PCN materials were collected under the same experimental conditions.

2.5. Thermogravimetric analysis and differential scanning calorimetry

The thermal stability of the PVA and PCN materials was evaluated by thermogravimetric analysis (TGA) using a Pyris 6 TGA (PerkinElmer) operated in air. The experimental conditions had a starting temperature of 30°C and final temperature of 900°C, with a heating rate of 10°C/min. The thermograms were collected using PerkinElmer software (2009). The mass reproducibility was $\pm 0.2\%$ and the temperature was ± 2°C during the TGA technique. The glass transition temperature (T_g) was evaluated by differential scanning calorimetry (DSC) technique using Jade DSC, PerkinElmer 2010, operated in nitrogen. The experimental conditions had a starting temperature of 30°C and a final temperature of 400°C, with a heating rate of 10°C/ min. The thermograms were collected using PerkinElmer software 2009. Each measurement was repeated and the mean taken to draw the thermograms.

2.6. Mechanical properties study

Samples were prepared from 7.7 grams of the PVA and PCN powder using the injection moulding technique, into dog-bone shapes. The samples were prepared at a moulding temperature of 30°C and melting temperature of 250°C. Ten dog-bone shaped samples were prepared and the mechanical properties of the samples studied using Lloyds tensile strength instrument. The dog-bone shaped samples have dimensions of 18.5 cm $\times$ 2 cm $\times$ 0.3 cm.

2.7. Nano scanning electron microscopy

Pure polyvinyl alcohol (PVA), pure MMT and the PCN materials were morphologically characterized by Nova™ NanoSEM Scanning Electron Microscope 450, FEI™, Netherlands. The NSEM operated at 1 kV for imaging and 20 kV for energy dispersive spectroscopy (EDS) and the samples were gold coated. The images were captured using Nova NanoSEM software (2010).

3. RESULTS

3.1. Structural morphology

The morphology of the clay-containing PVC systems was evaluated using a combination of XRD and nano-scanning electron microscope (NSEM). Figure 1a shows the XRD patterns of organophilic clay MMT and a series of PCN materials of 1%, 2%, 3%, 4%, 5%, 10%, 20% and 30%. The value of 2θ in the XRD pattern enables evaluation of the d-spacing of the intercalated structures, by evaluating how much expansion has occurred by entry of the polymer into the silicate layers of the clay. There are three possibilities: no change in the d-spacing of the clay, indicating no dispersion or no nanocomposite structure formation; 2θ value is observed to be shifted to a lower value, which indicates intercalated
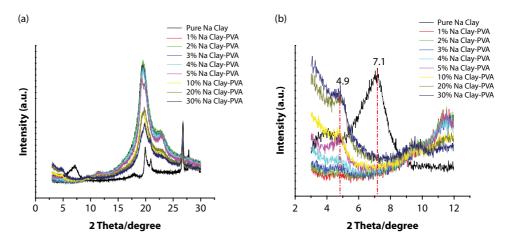
Figure 1. XRD patterns of bulk organophilic clay Na-rich Montmorillonite (black solid line) and different loading concentrations of organophilic clay (MMT) with polyvinyl alcohol (PVA). The loading concentrations are in the range of 1−30% w/w. The patterns were collected using desktop X-ray Rigaku Miniflex II diffractometer equipped with Cu-K$_\alpha$ source ($\lambda = 1.5404$ Å), Japan. It was operated at 50 kV and 20 mA. Scans were obtained in a 2θ range from 3° to 30° with a 2 step size.

structures in the nanocomposite; or finally, the XRD pattern does not exhibit peak or a broad peak, indicating a disordered structure (loss of parallel clay silicate layers stacking).[30]

Figure 1b shows the expanded range of the concerned part of the X-ray patterns. As seen, the X-ray profile of the nanocomposites has a characteristic diffraction peak at $2\theta = 4.9°$ (d-spacing = 1.8 nm) while this peak appeared at $2\theta = 7.1°$ (d-spacing = 1.244 nm) in the MMT clay X-ray profile. The decrease in the 2θ of the PCN in comparison to the 2θ value of the MMT clay, indicates that d-spacing of the PCN has increased. The d-spacing increase of Swy-2 MMT clay in the presence of PVA, implies that PVA has intercalated between the silicate layers of Swy-2 MMT during the solution method of the samples preparation.

Nano-scanning electron microscope (NSEM) is combined with the XRD to determine the microstructure of nanocomposites. Figure 2 shows sheet-like plates (flakes) of the MMT clay with
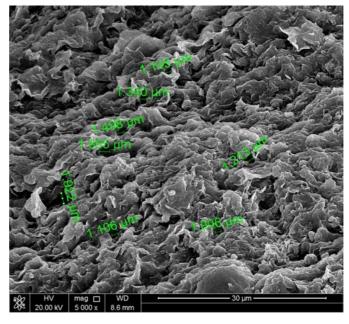

Figure 2. Nano-scanning electron microscope (NSEM) of the bulk organophilic clay Na-rich Montmorillonite and shows the sheet-like plates (flakes) of the clay with an average spacing distance of 1.4 μm.

average spacing distance of 1.4 μm. Figure 3 shows the PVA microscopic image and the average particles size diameter of 5 nm. Figure 4 shows that all the spacing distances of the MMT clay were covered by the PVA and that the PCN appears like a solid rock in one piece. This is due to the clay layers
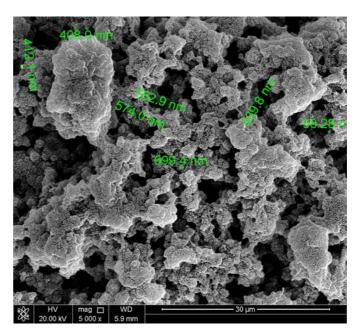
Figure 3. Nano-scanning electron microscope (NSEM) of bulk polyvinyl alcohol (PVA) with an average particle size diameter of 5 nm.
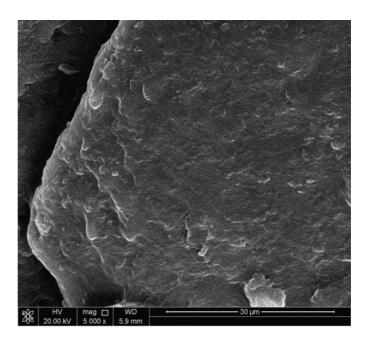

Figure 4. Nano-scanning electron microscope (NSEM) of the polymer-clay nanocomposite (PCN). The concentration of the MMT and PVA in the PCN is 5% and 95%, respectively.

dispersed uniformly and homogeneously in the polymer matrix and the interlayer spacing, which forms the basis of the intercalated morphology. These NSEM results were in agreement with the results of the XRD patterns. According to the results obtained from XRD and NESM, the MMT clay is intercalated with PVA, which is increasing the interlayer space of the MMT clay.

3.2. X-ray fluorescence

Figure 5 shows typical energy dispersive XRF spectrum of pure Montmorillonite clay. The spectrum shows that silicon (Si) has the highest element ratio in the MMT components. There are other elements with significant ratios such as Al, Mg, O, Ca and Fe.
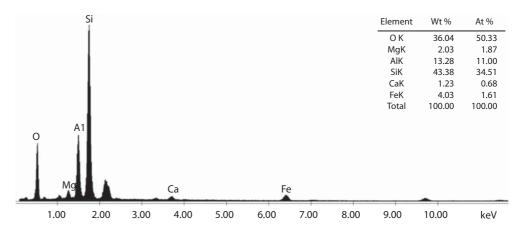
Figure 5. XRF spectrum of the bulk Na-rich Montmorillonite.

3.3. Thermal properties of polymer-clay nanaocomposite (PCN)

Figure 6 shows TGA thermograms of weight loss as a function of temperature for the PVA and PCN materials, as measured under nitrogen atmosphere. In general, major weight losses are observed in the range of ∼ 200–500°C for PVA and PCN fine powders, which may be correspondent to the structural decomposition of the polymers. Evidently, the thermal decomposition of the PCN materials shifts slightly toward the higher temperature range than that of the PVA. The results show that the PCN thermogram exhibits higher melting temperature than the PVA thermogram. The melting temperature of PCN starts at 250°C, while the melting temperature of PVA starts at 220°C. This result indicates the enhancement of the thermal stability of the intercalated polymer by nearly 14%. After 600°C, the curve becomes flat and mainly the inorganic residue (i.e. Al_2O_3, MgO, SiO_2) remains. The mass loss in the PVA was 7% and the mass loss in the PCN materials was 12%.
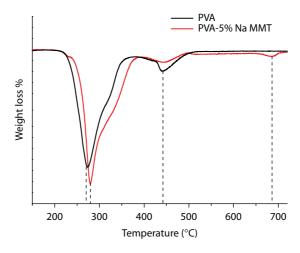

Figure 6. TGA thermograms of (a) bulk PVA, black line and (b) 5% MMT-PVA, red line.

Figure 7 shows DSC thermograms of the PVA and PCN materials. The figure shows that there is an endotherm at around 80°C in the DSC thermograms of PVA, which corresponds to the glass transition temperature (T_g) of PVA.[13] This T_g in the PCN materials thermogram is shifted to higher value compared to the bulk PVA of 95°C. The increase in the promoted polymer (PCN) T_g may be attributed to intercalation occurring by entry of the polymer chains into the gallery space of the clay and the polymer chains. The polymer chains are well-dispersed and confined within silicate layers of the MMT clay, resulting in the lack of segmental motions of the polymer chains.

DSC thermograms of the PVA and PCN materials exhibit the same endotherm at higher temperatures of 230°C, which corresponds to the crystalline melting point (T_m) of PVA. The PCN material thermogram exhibits a second higher T_m endotherm at 240°C. This result indicates that the PCN materials may develop two crystalline phases due to polymer-clay intercalation, which can result in the enhancement of the thermal stability of the intercalated polymer.
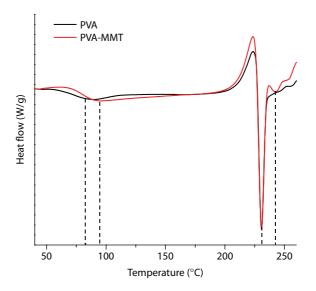
Figure 7. DSC thermograms of (a) bulk PVA, black line and (b) 5% MMT-PVA, red line.

3.4. Mechanical properties study

Room temperature mechanical properties were evaluated using a tensile tester. The average values of various tensile moduli from 10 dog bone samples are given in Tables 1 and 2 for PVA and PCN materials, respectively. The addition of the MMT clay in the PVA matrix markedly changes the yield point of the PVA polymer.

Table 1. Mechanical properties of PVA

Sample Name	Speed	Gauge Length	Width
PVA	10.000 mm/min	50.000 mm	12.500 mm
Thickness	Load at Maximum Load	Tensile Strength	Young's Modulus
3.0000 mm	267.6 N	7.1 MPa	521.6 MPa
Load at Break	Stress at Break	Work to Break	Percentage Total Elongation at Fracture
104 N	2.8 MPa	2590.5 Nmm	15.7

Table 2. Mechanical properties of polymer-clay nanocomposite (PCN) materials (PVA-MMT)

Sample Name	Speed	Gauge Length	Width
Polymer-clay nanaocomposite (PCN) materials (PVA-MMT)	10.000 mm/min	50.000 mm	12.500 mm
Thickness	Load at Maximum Load	Tensile Strength	Young's Modulus
3.0000 mm	2297.3 N	61.3 MPa	2183.3 MPa
Load at Break	Stress at Break	Work to Break	Percentage Total Elongation at Fracture
2212.5 N	59 MPa	4506.8 Nmm	22

The results show an improvement in the tensile moduli of the PVA polymer after adding the MMT clay. The Young's Modulus of the PVA and the PCN were given the values of 521.58 MPa and 2183.3 MPa, respectively. The results also show that maximum load for the PCN of 2297.3 N is higher than the PVA value, 267.57 N. The results show that the work required to break the PCN is 4506.8 Nmm and is higher than the PVA value of 2590.5 Nmm. The addition of 5 wt% MMT clay to PVA increases the elongation at break of the PVA polymer from 5% to 22%. The addition of a small amount of the clay enhances the ductility of the PVA matrix. The tabulated results showed that the moduli of the intercalated polymer are higher than the pure PVA polymer, which indicates that the tensile modulus of PVA is promoted as clay loaded. Improvement of the tensile moduli will make the promoted PVA exhibit reinforcement behavior based on its stiffness and high-performance values.[31,32−36]

4. DISCUSSION AND CONCLUSION

Solution method was used to prepare a series of PCN with different concentrations of layered MMT clay. This preparation method helped in dispersing the inorganic nanolayers of MMT clay in organic PVA matrix and the PVA polymer chain between the silicate layers of the MMT clay. The PCN are characterized by XRD and NSEM as well as measurements of their mechanical properties.

NSEM morphological images of PCN materials indicated that intercalation between PVA and MMT occurred. The crystalline morphology studies using the XRD of the clay showed that the *d*-spacing between the MMT clay layers increases in the presence of PVA. The broadening and diffusing of the XRD peak of the PCN materials indicated that both intercalated/exfoliated structures were present. Also, pure PVA tends to have amorphous state as the MMT clay loading increases. The morphological images and crystalline morphology indicated that PVA and MMT clay has intercalated by the uniform and homogenous dispersion and confinement of the PVA polymer chains within silicate layers of the clay during the solution method of the samples preparation. The result is in agreement with previous XRD studies for PVA/MMT nanocomposites which showed excellent dispersion of the clay particles into the polymer matrix resulting in the formation of exfoliated and intercalated structures. The polymer−clay interactions enhance the overall material performance such as improving the mechanical strength and increasing the heat resistance of the PCN.[37] These results compare to those obtained by Strawhecker and Manias in 2000, which showed that XRD results of PVA/MMT nanocomposites formed by a solution method show a coexistence of exfoliated and intercalated silicate layers.[13]

The excellent MMT nanoclay dispersion in the PVA matrix leads to significantly enhanced mechanical properties, notably an increase in tensile moduli with significant increase in tensile strength, maximum load, work to break and percentage elongation of the PVA due to adding a small amount of MMT clay. Adding small amount of inorganic clay to the PVA polymer creates a PCN that exhibits increased toughness and a higher-performance polymer, expressed by higher values of mechanical property parameters. Furthermore, the promoted (intercalated) PVA polymer has higher ductility than the pure PVA material, which can produce a high threshold of break and good shock absorbance. Assessment and evaluation of the thermal stability and mechanical strength of PVA and a series of PCN materials showed the effect of the inorganic nanoclay on the PVA polymer. The uniform and homogenous dispersion of nanolayers clay (MMT) in PVA matrix results in an increase in thermal decomposition temperature and glass transition temperature of the promoted PVA polymer based on TGA and DSC results. The result is in agreement with the previous DSC thermal studies of the PVA/MMT nanocomposites that showed low MMT loading nanocomposites exhibiting a new melting transition with higher T_m than the neat PVA. The mechanical/tensile properties of the PVA/MMT nanocomposites were also obtained, and Young's modulus was found to increase by 300% for 5 wt % silicate compared to neat PVA. In addition, for low loadings, thermal stability from TGA measurements was shown to be slightly enhanced.[13]

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