Mechanical Properties of Poly(vinyl alcohol) Montmorillonite Nanocomposites

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ABSTRACT: The properties of polymers are greatly enhanced when they are incorporated with silicate-layered clays as they find many applications in the fields of electronics, automobile industry, packaging, and construction. In this study a thermoplastic polymer poly(vinyl alcohol) (PVA) and montmorillonite (MMT) clay were used to prepare MMT-PVA nanocomposites and their mechanical properties were investigated. In general PVA is used in paper coating and packaging where their tensile strength and tearing strength are vital. The MMT-PVA nanocomposites displayed more than 60% increase in the tensile strength and young's modulus where as the tearing energy doubles the value of neat PVA. This is a substantial enhancement compared to that reported so far. The enhancement was achieved at low clay content probably due to its exfoliated structure. The dispersed clay layers are well embedded with PVA matrix via strong interatomic interactions leading to better material properties.

KEY WORDS: MMT-PVA nanocomposites, tensile strength, Young's modulus, tearing strength, double edge notched tension.

INTRODUCTION

CLAY POLYMER NANOCOMPOSITES (CPNs) represent a new class of material alternative to conventionally filled polymers in which nano-sized inorganic fillers are dispersed in polymer matrix, offering tremendous improvement in the properties of the polymer. The improvements in material properties such as elastic modulus, strength, thermal stability, fire retardancy, gas barrier properties, and solvent resistance over traditional polymers have made CPNs as attractive alternative for use in the packaging and

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automotive industries [1–5]. Typically smectite-type clays having 2:1 layered structures are used as fillers. Montmorillonite (MMT), hectorite, and saponite are the most commonly used layered silicates. Isomorphic substitution within the layers (e.g., Mg^{2+} replaces Al^{3+}) generates negative charges that are normally counterbalanced by hydrated alkali or alkaline earth cations residing in the interlayer. Because of the relatively weak forces between the layers (due to the layered structure), intercalation of various molecules, even polymers, between the layers are facile [6–10]. In CPN, polymer molecules can intercalate into the galleries in layered silicates, pushing the layers apart and creating a nanocomposite with high aspect ratio [11]. Depending on the nature of the components used (layered silicate and polymer matrix) and the method of preparation, three main types of composites can be obtained when layered clay is associated with a polymer. They are phase-separated microcomposites, intercalated nanocomposites, and exfoliated nanocomposites [12].

Poly(vinyl alcohol) (PVA) is a water-soluble polymer extensively used in paper coating, textile sizing, and flexible water-soluble packaging films [13]. These same applications stimulate an interest in improving mechanical properties of thin PVA nanocomposite films. There are several publications associated with the MMT-PVA nanocomposites and their mechanical properties [14,15]. Chang et al. reported 50% of increase in the tensile strength and 30% increase in the Young's modulus and Giannelis et al. reported a 25% increase in the tensile strength for 4 wt% of MMT clay. The tearing energy of PVA–clay nanocomposite materials prepared by solution-intercalation film-casting has not been reported elsewhere.

The present work explores first the structure of MMT-PVA nanocomposite materials spanning the complete range of inorganic (MMT) loadings. Subsequently, this study focused on a comparative study of the mechanical properties of pure PVA and MMT-PVA nanocomposites, with the emphasis on the application relevant, a range of MMT concentration (2–10 wt%) hybrid materials.

EXPERIMENTAL

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 (meq) per 100 g, has high aspect ratio and can swell 14–16 times upon hydration. Bentonite, which is pale yellow in color, has a molar mass of 540.46 g/mol and has a density of 2.35 g/mL. PVA was purchased from Aldrich chemicals, which has the density of 1.28 g/mL and is of high purity. These PVA are white free-flowing granules in appearance and used as it is.

Preparation

MMT-PVA nanocomposites were synthesized by a solution-intercalation film-casting method: hybrid films were cast from MMT water suspension where PVA was dissolved. Room temperature distilled water was used to form a suspension of sodium montmorillonite (MMT) at a concentration of ≤2.5 wt%. The suspension was stirred for 1 h. Low-viscosity, fully hydrolyzed (98.0–98.8%) atactic PVA was added to the stirring suspensions

so that the total solids (silicate plus polymer) concentration was ≤ 5 wt%. The mixtures were then heated to 90°C to dissolve the PVA and stirred for 30 min, and finally films were cast in a closed oven at 40°C for 1 day. Various compositions with different clay content were prepared (2, 4, 6, 8, 10 wt%) with constant polymer content.

Characterization

X-ray diffraction (XRD) spectra (Seimens D-5000, radiation Cu Kα $\lambda = 0.1540562$ nm) were recorded for raw MMT, neat PVA, and the PVA-MMT series of composition at ambient laboratory temperature. Samples for the XRD scanning were prepared by forming thin films on clean glass plates.

Testing of Properties

Mechanical properties were investigated by using a 'Mechanical testing machine.' Tensile strength, Young's modulus (Y), double edge notched tension (DENT), and two-leg trouser tearing strength (TS) were investigated [16]. The test specimens were prepared according to the film thickness and the dimensions were kept constant for all the composition, as there is no indication of ASTM standards for MMT-PVA nanocomposites. Tensile test samples were prepared by cutting pieces from the cast films with a gage dimension of $21 \times 7 \times 0.2$ mm^3. The mechanical testing machine was used at a speed of 0.3 mm/s to pull the sample from both ends and the force required to break the specimen apart was found to determine the tensile strength. The Young's modulus of the MMT-PVA nanocomposites was found by the tensile specimen elongation and applied force. Two types of fracture tests have been carried out on the MMT-PVA nanocomposite films. They were mode I fracture test using DENT specimen and two-leg trousers tear test.

DENT test was performed using the mechanical testing machine at a speed of 0.3 mm/s for the rectangular MMT-PVA test films (Figure 1(a)) of dimension $40 \times 15 \times 0.2$ mm^3 consisting of two notches at each sides of its length. The stress intensity factor was calculated from the maximum breaking load using the Equation (1) [17]:

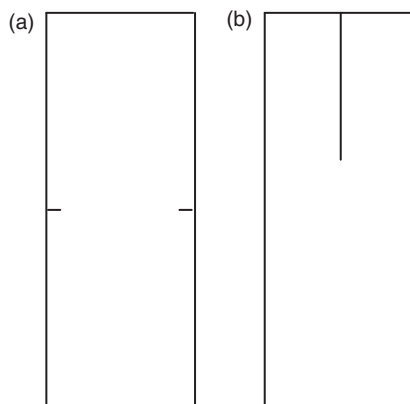$$K_{1c} = Y\sigma\sqrt{\pi c}, \qquad (1)$$

Figure 1. *(a) DENT specimen, (b) two-leg trouser tear specimen.*

where K_{1c} is the fracture toughness measured in MPa m$^{1/2}$, σ is the applied stress, c is the crack length, and Y is a geometrical factor, which depends on the crack and sample geometry. For DENT test:

$$Y = 1.12 + 0.203\left(\frac{a}{b}\right) - 1.197\left(\frac{a}{b}\right)^2 + 1.93\left(\frac{a}{b}\right)^3. \tag{2}$$

The tear resistance of the packaging materials is also very important. The specimen is a thin rectangular piece cut centrally along its length to form two legs (Figure 2(b)). The legs were pulled in opposite directions out of the plane of the test piece by equal and opposite forces. The expression for tearing energy is:

$$T = \frac{2\lambda P}{h} - 2bw, \tag{3}$$

where P is the force on the legs of the specimen, λ the extension ratio in the legs (ratio of length of deformed to undeformed leg), h the specimen thickness, b the width of the legs, and w the strain energy density in the legs. While the specimen legs can be considered inextensible compared with the tearing ($\lambda \cong 1, W \cong 0$), Equation (3) is simplified as:

$$T = \frac{2P}{h}. \tag{4}$$

The trouser tear test was carried out for MMT-PVA and K-PVA composites at a crosshead speed of 0.3 mm/s and at a constant temperature of 28°C. The tearing energy was calculated according to Equation (4).
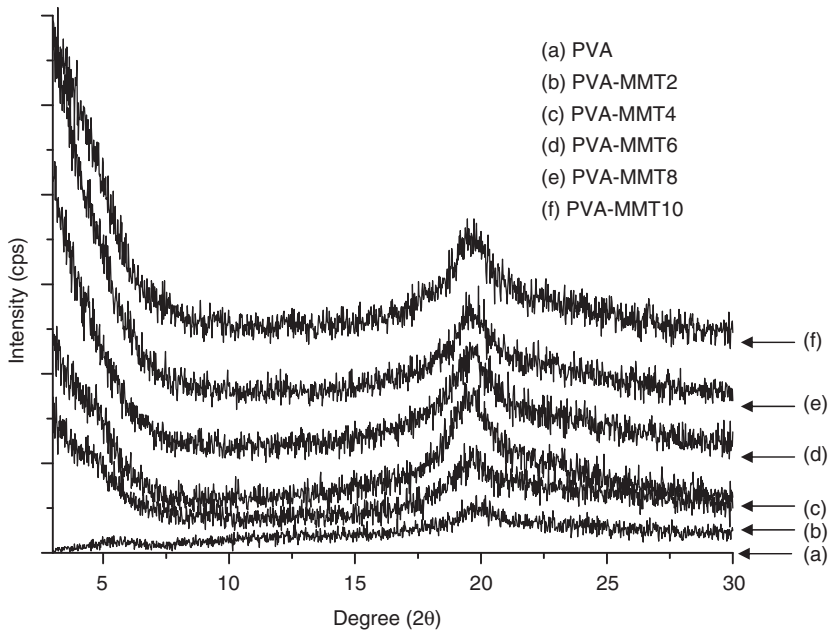

Figure 2. XRD spectra of the PVA-MMT series at ambient laboratory conditions.

RESULTS AND DISCUSSION

Characterization

The XRD revealed (Figure 2) that the d-spacing decreases gradually with the increasing clay content (Table 1). The XRD peak that corresponds to lower clay content shifted slightly less than 3° and if there still exists periodic assemblies of intercalated MMT layers, those are characterized by d-spacing larger than 28 Å. This result indicates the existence of exfoliated inorganic layers throughout the polymer matrix and the degree of exfoliation decreases with increasing clay content.

Mechanical Properties

Mechanical properties are controlled largely by the interatomic forces or the interatomic potential energy. CPN shows enhanced mechanical properties compared to their virgin materials or their microcomposite. In this work tensile strength, Young's modulus (Y), and the mode III fracture toughness (K_{IIIc}) were investigated and presented for the MMT-PVA nanocomposites.

TENSILE STRENGTH

The ultimate tensile strength of the MMT-PVA nanocomposite for different clay contents is shown in Figure 3. The results show that the tensile strength increases by 62% of the value of the neat PVA. There is an achievement of 12% of enhancement compared to that reported in literature. This enhancement is achieved for the nanocomposites, which have low clay contents and tends to level off for higher clay loading. Particularly nanocomposite with 4 wt% of clay has a strength that is 1.6 times greater than the strength of the neat polymer. The improvement is mainly due to the reinforcement gained by the good dispersion of the nano-sized inorganic clay layers in the polymer matrix and their interatomic interactions yield through the strong interaction between the polymer matrix and silicate layers via the formation of hydrogen bonds.

The number of flaws existing in the nanocomposite including the weak boundaries between particles and the bubbles trapped during the sample preparation may increase with the increasing clay content, which cause the decrement in strength for the nanocomposites that have higher clay content [10–12]. Inhomogeneous dispersion of the clay contributes aggregates of particles to the matrix, which is also increasing with increasing clay content. The stress field in the vicinity of the aggregate will be high, resulting in easier crack initiation and propagation, and consequent failure at low fracture level.

Table 1. The d-space of PVA-MMT nanocomposite.

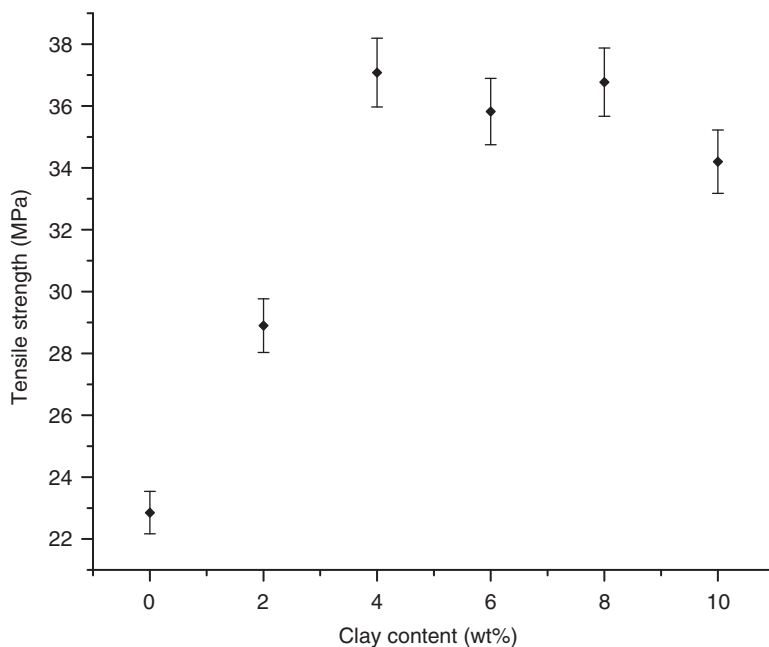| MMT-PVA nanocomposite	Clay content (wt%)	d-spacing (Å)
PVA-MMT2	2	28.84
PVA-MMT4	4	29.22
PVA-MMT6	6	28.1
PVA-MMT8	8	27.93
PVA-MMT10	10	27.75
MMT	100	15.43

Figure 3. Tensile strength of the MMT-PVA nanocomposites averaged of five tests.

YOUNG'S MODULUS

The Young's modulus (Figure 4) increased by 61% for the nanocomposites with low clay contents and shows no significant increase for higher clay contents. This result shows 11% of enhancement when comparing the existing research literature. The clay layers are affected by the polymer on its surface, with a much higher Young's modulus than the bulk equivalent polymer. As the MMT clay has only one dimension in the nano size the surface area of the MMT clay exposed to polymer is typically large (for MMT it is 7×10^5 to 8×10^5 m^2/kg) and hence the increase in the modulus [1–3].

Beyond the 4 wt% of the clay the compositions may have aggregates of MMT layers, and thus it is expected that the enhancement of the Young's modulus will be much less significant.

MODE III FRACTURE TOUGHNESS

The toughness of a material is generally related to the energy dissipating events that occur in the vicinity of a sharp crack. The two-leg trouser tearing energy (Figure 5) of the MMT-PVA nanocomposite was radically increased for low clay contents and gradually decreasing for higher clay loadings. For 4 wt% of MMT-PVA system the tearing energy is twice as that of neat PVA. The tore specimens of MMT-PVA nanocomposites are shown in Figure 6. The specimens that had diagonal tear were discarded.

In the MMT-PVA nanocomposite, the microvoids might be responsible for high toughness. These microvoids release the plastic constraint in the matrix, triggering large-scale plastic deformation with consequent tearing of matrix ligaments between microvoids. While in the neat PVA, only crazing contributes to energy absorption, which is low in comparison.
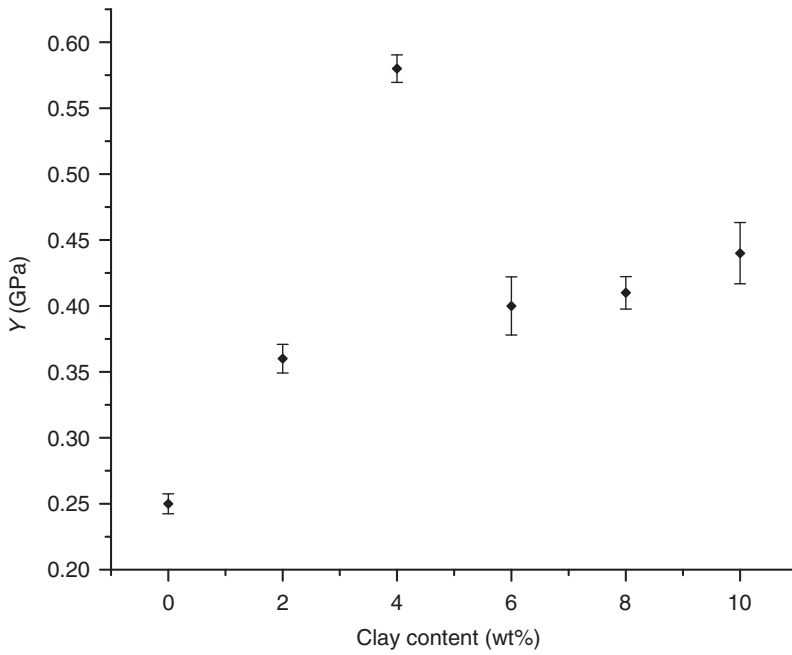
Figure 4. *Young's modulus of the MMT-PVA nanocomposites for different clay contents averaged by five tests.*
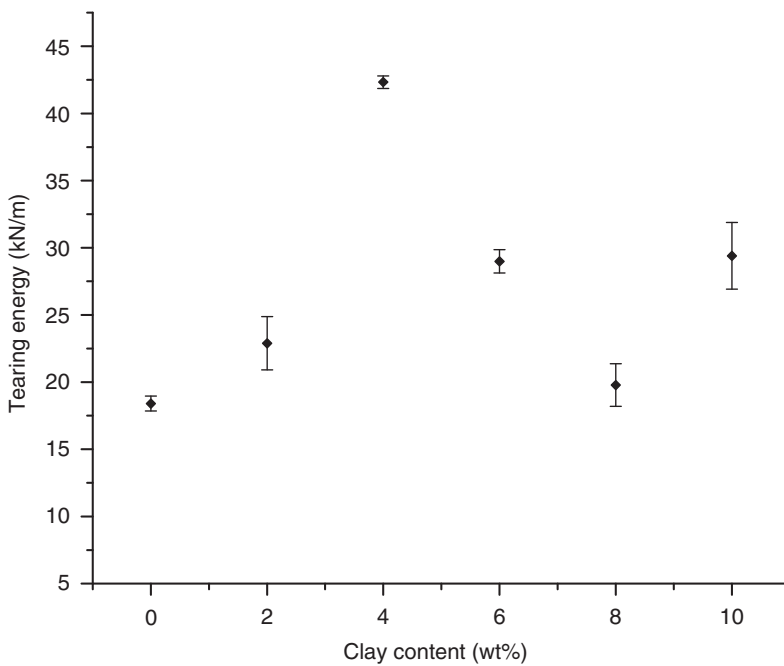

Figure 5. *Two-leg trouser tearing energy of the MMT-PVA nanocomposites averaged by five tests.*
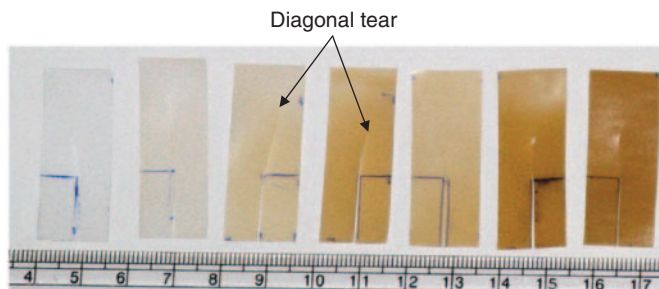
Figure 6. Two-leg trouser tearing specimens of the MMT-PVA nanocomposites.

The higher clay contents increase clay aggregates that resulted in brittle fracture. Thus, the nucleation of microvoids has a positive effect in the enhancement of tearing energy while the agglomeration of clay particles has a negative effect [18].

CONCLUSION

The results indicate that the mechanical properties significantly increased for the MMT-PVA nanocomposites at rather low clay content compared to their neat counter parts. The large surface area, better dispersion, and the degree of exfoliation of the MMT clay contributes to the enhancement while the trapped air bubbles and the clay aggregates may decline the mechanical properties.

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