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POLYVINYL ALCOHOL/SILICA/CLAY COMPOSITES: EFFECT OF CLAY ON SURFACE MORPHOLOGY AND THERMO-MECHANICAL PROPERTIES

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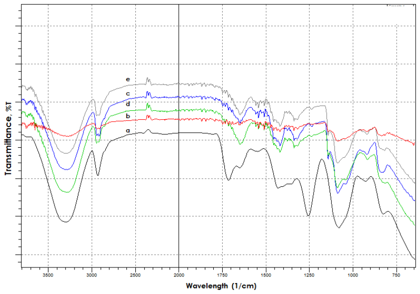
Graphical abstract



Abstract

A simplified route towards the synthesis of polyvinyl alcohol/silica/clay (PVA-SiO_2-clay) composites was presented. PVA-SiO_2-clay composites were prepared via solution intercalation method. All the composites were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), adsorption isotherm (BET), X-ray fluorescence (XRF), tensile test and Thermogravimetric Analysis (TGA). FTIR spectrum indicated that PVA-SiO_2-clay composites especially clay (1.28E) loaded composites had much less transmittance percentage compared to pure PVA and others clay composites. The SEM revealed that the interfacial bonding between PVA-SiO_2 and clay (1.28E) was much better than others clay loaded composites which was reflected in adsorption isotherm. The BET result also showed high specific surface area with low diameter of pore size of the composites. The thermal stability of PVA-SiO_2-clay (1.28E) composites was the highest and it had higher activation energy due to the strong bonding between the trimethyl stearyl ammonium with both PVA-SiO_2. The XRF result showed that clay (1.28E) loaded composites contained significant high percentage of Si which confirmed the presence of Si-O-Si stretching vibration while the high percentage of K proved the clay mineral content in the composite. Clay (1.28E) enhanced the tensile strength and modulus of PVA-SiO_2-clay composites among all the composites.

Keywords: Polyvinyl alcohol/silica/clay composites, FTIR, SEM, TGA, XRF, BET

Abstrak

Satu laluan yang termudah untuk sintesis komposit polivinil alkohol/silika/tanah liat (PVA-SiO_2-tanah liat) telah dibentangkan. Komposit PVA-SiO_2-tanah liat telah disediakan melalui kaedah penyelesaian interkalasi. Semua komposit telah disifatkan melalui Fourier Transform Infrared Spektroskopi (FT-IR), Mengimbas Mikroskopi Elektron (SEM), penjerapan isoterma (BET), sinar X pendarfluor (XRF), ujian tegangan dan Analisis Termogravimetri (TGA). Spektrum FTIR menunjukkan bahawa komposit PVA-SiO_2-tanah liat terutamanya komposit muatan tanah liat (1.28E) mempunyai kurang peratusan pemindahan berbanding dengan tulen PVA dan komposit muatan tanah liat yang lain. SEM mendedahkan bahawa ikatan antara PVA-SiO_2 dengan tanah liat (1.28E) adalah jauh lebih baik daripada komposit muatkan tanah liat yang lain seperti dicerminkan dalam penjerapan isoterma. Hasil BET juga menunjukkan bahawa komposit mempunyai kawasan permukaan tertentu yang tinggi dengan diameter saiz liang yang rendah. Kestabilan haba komposit PVA-SiO_2-tanah liat (1.28E) adalah tertinggi dan ia mempunyai tenaga pengaktifan yang lebih tinggi kerana ikatan yang kuat antara ammonium trimethyl stearyl dengan kedua-dua PVA-SiO_2. Hasil XRF menunjukkan bahawa komposit muatan tanah liat (1.28E) mengandungi peratusan Si yang tinggi telah mengesahkan kehadiran getaran regangan Si-O-Si manakala peratusan tinggi K membuktikan kandungan mineral tanah liat dalam komposit. Tanah liat (1.28E) meningkatkan kekuatan tegangan dan modulus komposit PVA-SiO_2-tanah liat antara semua komposit.

Kata kunci: Polivinil alkohol/silika/tanah liat komposit, FTIR, SEM, TGA, XRF, BET

1.0 INTRODUCTION

Polyvinyl alcohol (PVA) is one of the most widely used polymers due to its unique properties. PVA can be prepared using the polymerization of vinyl acetate followed by alcoholysis. It is a polyhydroxyl compound that has been widely used making films, fibers, paper coating, articular cartilage, thickener materials in paints, detergent and adhesives due to its with excellent biocompatibility and attractive properties [1]. Besides, good mechanical and thermal properties makes PVA become one of the most widely used polymers in paper coating, textile sizing and flexible water-soluble packaging films fields [2]. However, PVA is strongly hydrophilic and soluble in water as the hydroxyl (-OH) groups located on alternating carbon atoms in its structure. Due to the hydrophilic nature, PVA can be degraded through the hydrolysis [3]. Nowadays, PVA composites has become one of the main research interests due to their potential applications in biomedical devices, drug delivery systems, carrier for cells immobilization, carrier for signaling molecules and bioseparation membranes [4].

Nowadays, micro silica is widely used as a pozzolanic admixture that is effective in enhancing the mechanical properties to a great extent [5]. Silica is defined as very fine non-crystalline silica produced in the electric arc furnaces as a byproduct of production of elemental silicon. Silica particles play an important role when it is embedded in a polymer matrix for its large surface area and smooth nonporous surface [6].

Clay is defined as a class of materials made up of layered silicates. The most commonly used clay is montmorillonite (MMT) that has been improving the physical and mechanical properties of composites [7]. The importance of organic alkyl exchanged clay is to enhance its hydrophobicity. Besides, it can help to expand the interlamellar spaces of silicate platelets [8]. Nanomer, Nanoclay 1.28E will help to enhance tensile strength and thermal properties of the composites formed. Besides, Nanomer, Nanoclay 1.30E is designed to be easily dispersed in resins to form composites and helps to improved performance at minimal added weight. Nanomer, Nanoclay 1.31PS contributes better dispersion, heat stability and mechanical properties while Nanomer, Nanoclay 1.34TCN enhances mechanical properties at low loadings and minimizes the surface imperfections compared to the conventional fillers [9]. However, the incompatibility between hydrophilic clay and hydrophobic polymer is the drawback, which often causes agglomeration of clay mineral in the polymer matrix [10].

Composite materials are defined as combination of two or more different compounds such as polymers, glass and ceramics. Polymer composites can be explained as the polymers or copolymer having materials as dispersed phases in its.

PVA/clay composite hydrogels can be apply on wound dressing as it can meet the essential requirement such as good mechanical properties [11]. Besides, 1% nanoclay acts as a filler is added into PVA/starch matrix shows that the maximum strength of the composites. However, the transparency of the composites decreases as the clay is added to the matrix. This proves that 1% nanoclay is the optimum clay loading towards PVA/starch matrix [12]. In addition to that, the dispersion of 25 vol.% MMT into pure PVA to form composites shows that TGA decomposition rate decreased as the MMT concentration increased. This proves that thermal stability of PVA/MMT composites increases as MMT acts as reinforcing particles. Besides, the composites shows significant improvement in tensile strength at low clay loading and loading rate compared to the pure PVA. However, the tensile strength decreases when the clay loading and its loading rate increases. This shows that there is limitation of the clay loading into PVA matrix [13].

Polymer/silica nanocomposite is another area that gained a lot of attraction from both academician and industrial researchers due to their excellent electrochemical performance, proton conductivity, higher tensile strength and thermal stability. The SEM micrographs of PVA/silica composites show that silica was dispersed in the PVA matrix without the large aggregation of particles. Besides, PVA/silica composites are stronger and more useful than pure PVA with the addition of silica into PVA matrix. Therefore, PVA/silica composites are thermally stable with high tensile strength by sol-gel method [14].

In this study, micron size silica is used with different types of clay due to their extremely small dispersed particle size. Besides, both silica and clay have same interaction which creates a thixotropic system with shear thinning behavior [9]. The present study investigates the effect of different types of clays on physical, mechanical and thermal properties of PVA-SiO_2-clay composites. Throughout this study, the compatibility between clays and PVA-SiO_2 matrix is also investigated.

2.0 EXPERIMENTAL

2.1 Materials

The silica powders used in this study was obtained in a mesh size of 38 microns. The chemicals used (PVA, Nanoclay, Nanomer 1.28E, 1.30E, 1.31PS and 1.34TCN) were supplied by Sigma-Aldrich. Nanomer 1.28E is montmorillonite clay surface was modified with 25-30 wt.% trimethyl stearyl ammonium. The bulk density of the clay was 200 to 500 kg/m^3 and average particle size was around 20 microns. Nanomer 1.30E is montmorillonite clay was surface modified with 25-30 wt.% octadecylamine. The bulk density of that clay was 200 to 500 kg/m^3 and average particle size was around 20 microns. Nanomer 1.31PS montmorillonite clay surface was modified with 15-35 wt.% octadecylamine and 0.5-5wt.% aminopropyl triethoxysilane. The bulk density of the clay was 200 to 500 kg/m^3 and average particle size was around 20 microns. On the other hand, Nanomer 1.34TCN is montmorillonite clay surface was modified with 25-30 wt.% methyl dihydroxyethyl hydrogenated tallow ammonium. The bulk density of the clay was 200 to 500 kg/m^3 and average particle size was around 20 microns.

2.2 Methods

2.2.1 Preparation and Solution Intercalation of the Monomer Systems

The monomer system was prepared using PVA without using any initiator. 27 g of polyvinyl alcohol, 0.5 g of clay and 2.5 g of silicate powder were mixed initially as shown in Table 1. Silica was dried at 200°C for 48 hours in a vacuum oven. Polyvinyl alcohol and clay were dried at 50 and 60°C respectively for 24 hours in a vacuum oven. The samples were prepared in a deionized water/methanol (3:1) solvent mixture. The mixtures were first stirred at 70°C for 24 hours. Then, homogeneous solutions were ultrasonicated in an ultrasonic bath at room temperature for 1 hour. The solid films were produced by casting a sample onto a glass mold by slowly evaporating the solvent in air for 3 days. The films with a thickness of ~150μm were put in a vacuum oven at 50°C for 24 hours in order to get rid of the extra solvent. The dried films were stored in desiccators prior to characterization.

Table 1 Preparation of monomer system with different types of clay

Amount of polyvinyl alcohol (g)	Amount of silicate powder (g)	Amount (g) and type of clay
30	0	0
27	2.5	0.5 (1.28E)
27	2.5	0.5 (1.30E)
27	2.5	0.5 (1.31PS)
27	2.5	0.5 (1.34TCN)

2.3 Microstructural Analysis

2.3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The infrared spectra of the monomer systems were recorded on a Shimadzu IRAffinity-1. The transmittance range of the scan was 700 to 4000cm^1.

2.3.2 X-ray Fluorescence (XRF)

For each sample, scanning was conducted with a DP-6000 Delta Premium PXRF (Olympus, Waltham, MA, USA). The instrument features a Rh X-ray tube operated at 10-40 kV with integrated large area silicon drift detector (165eV). The instrument was operated in Geochem Mode which is capable of detecting the following suite of elements: V, Cr, Fe, Co, Ni, Cu, Zn, W, Hg, As, Se, Pb, Bi, Rb, U, Sr, Y, Zr, Th, Mo, Ag, Cd, Sn, Sb, Ti, Mn, Mg, Al, Si, P, S, Cl, K and Ca. Geochem Mode consists of two beams which operate sequentially. Each beam was set to scan for 30 s such that one whole scan was completed in 60 s. Prior to sample analysis, the XRF was standardized with a "316" alloy clip, tightly fitted over the aperture. Each soil was scanned in triplicate to obtain an average elemental composition for each sample; the XRF was repositioned between each scan. Elemental data was logged for each element, along with the limit of detection, defined as three times the standard error.

2.3.3 Scanning Electron Microscopy (SEM)

The interfacial bonding between the polyvinyl alcohol, clay and silicate were examined using a scanning electron microscope (SEM) (JSM-6710F) supplied by JEOL Company Limited, Japan. The specimens were first fixed with Karnovsky's fixative and then take through a graded alcohol dehydration series. Once dehydrated, the specimen was coated with a thin layer of gold before being viewed microscopically. The micrographs were taken at magnifications ranging from 250 to 1500.

2.3.4 Adsorption Isotherm

The nitrogen adsorption isotherm of PVA and PVA-SiO_2-clay composites at 77K was obtained by using a Quantachrome, Asic-7 physicosorption analyzer. In the analysis, the composites were degassed at 250℃ in vacuum for 1h before the nitrogen adsorption isotherm was constructed. The surface area and pore volume of composites was evaluated by the Brunauer-Emmett-Teller (BET) model.

2.3.5 Tensile Testing

Mold shape thin films were cut with a rectangular die and tested in a Lloyd LRX (2500N) materials testing machine at room temperature. The gauge length, width and thickness of the samples were 15, 2 and 0.15 mm respectively. The cross head speed used was 1mm/min. The quoted results were averaged over at least five specimens.

2.3.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) measurements were carried out on 5-10mg of both pure PVA and PVA-SiO_2-clay composites at a heating rate of 10℃/min in a nitrogen atmosphere using a Thermogravimetric Analyzer (TA Instrument SDT Q600). Pure PVA and PVA-SiO_2-clay composites were subjected to TGA in high purity nitrogen under a constant flow rate of 5mL/min. Thermal decomposition of each sample occurred in a programmed temperature range of 0℃ to 700℃. The continuous weight loss and temperature were recorded and analyzed.

3.0 RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The IR spectra of PVA and PVA-SiO_2-clay composites are shown in Figure 1. The characteristic peaks between 1100-1000cm^{-1}, 950-900cm^{-1} and 800-700cm^{-1} attributed to v(Si-O-Si), v(Si-OH) and δ(Si-O-Si) respectively. The characteristic band 1650cm^{-1} and 1420cm^{-1} are for v(C=C) and δ (CH_2) respectively. The IR spectrum of 2900 to 3100 cm^{-1} is attributed to v(CH_2) [15]. According to the finding, partial loss of silanol groups bonded with silica particles, which is detected and immobilized of vinyl groups on the surface of functionalized silica particles [16].

From Figure 1, the amplitudes for silanol groups bonds of silica particles decrease on vinyl silica particles (950-900cm^{-1}). However, the amplitudes of Si-O-Si are increased compared to the original silica particles as the clay and polyvinyl alcohol had coupled with silica particles. All of the characteristic peaks prove that polyvinyl alcohol and clay had reacted with silica.

The characteristic bands of PVA are v(O-H) at 3290cm^{-1} and v(C-H_2) at 2947cm^{-1}. There are major vibration bands at 950-900cm^{-1} and 800-700cm^{-1} appeared at PVA-SiO_2-clay composites. The peaks between 3500 and 3000cm^{-1} are mainly related to hydroxyl groups. It was noted that IR spectrum for PVA-SiO_2-clay (1.28E) composite had the least transmittance percentage with difference of 4% at 3290cm^{-1} and 2% at 2947cm^{-1}. The transmittance percentage of pure PVA, PVA-SiO_2-clay (1.30) composite, PVA-SiO_2-clay (1.31PS) composite and PVA-SiO_2-clay (1.34TCN) composite at 3290cm^{-1} are 32%, 28%, 30% and 16%. At 2947cm^{-1}, the transmittance range for pure PVA, PVA-SiO_2-clay (1.30) composite, PVA-SiO_2-clay (1.31PS) composite are 6% respectively and 4% for PVA-SiO_2-clay (1.34TCN) composite. The silica particles appeared at side chain hampered the formation of hydrogen bond between PVA chains. From this result, it is successfully proved that polyvinyl alcohol and clay are compatible with silica and has altered PVA chains tri-dimensional structure [16].

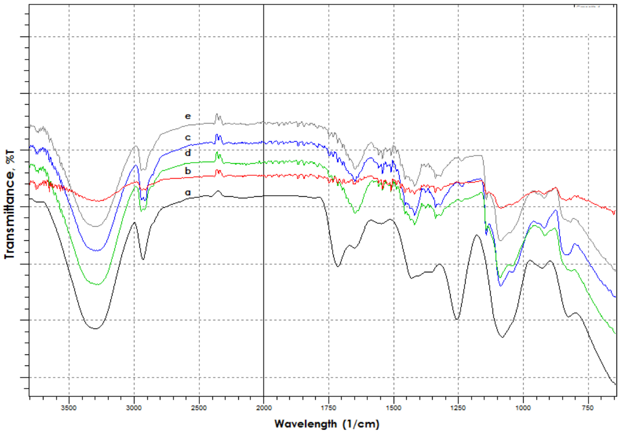


Figure 1 FTIR spectra of (a): PVA, (b) PVA-SiO_2-clay (1.28E) composite, (c) PVA-SiO_2-clay (1.30E) composite, (d) PVA-SiO_2-clay (1.31PS) composite and (e) PVA-SiO_2-clay (1.34TCN) composite

3.2 X-ray Fluorescence (XRF)

It is performed to know the compositions of the minerals that are present in the pure PVA and PVA-SiO_2-clay composites as shown in Table 2. The composites contain silicon, calcium and iron in major quantities and other elements in minor quantities [17]. It is obvious that improvement on the chemical composition of clay as result of beneficiation is marginal. The infrared and compositional analyses indicate that the clay particles fit into the PVA-SiO_2 system. From Table 2, it shows that pure PVA does not contain any silica particles while PVA-SiO_2-clay composites contain high percentage of silica group which confirmed the presence of silanol group as silanol group was assigned to Si-O-Si stretching vibration and high percentage of K proved the clay mineral content in the composites [18]. Therefore, the appearance of silica group improves the thermal and mechanical properties of the composites in comparison to the pure PVA.

Table 2 Oxide Content of PVA and PVA-SiO_2-clay composites

Sample	Si	Ca	Fe	S	Cr	K	Cu
PVA		30.3	36.6				32.9
PVA-SiO_2-clay (1.28E)	40.9	33.0	15.0	1.7	1.7	2.5	
PVA-SiO_2-clay (1.30E)	32.7	32.3	26.3	4.4	2.2	1.7	
PVA-SiO_2-clay (1.31PS)	31.4	34.0	22.9	1.7	2.2	2.1	
PVA-SiO_2-clay (1.34TCN)	33.3	35.2	21.5	6.5	2.1	1.2	

3.3 Surface Morphology

The SEM micrographs of pure PVA and PVA-SiO_2-clay composites are shown in Figure 2 (a-e). From Figure 2(a), the pure PVA displays a smooth surface, which indicates that there is no interfacial bonding due to the absence of monomer intercalation [15]. Figure 2 (b-e) shows some agglomeration between PVA, silica and clay proving aggregation of silica in the inter-spherulitic region (amorphous region). The uniform surface of PVA-SiO_2-clay (1.28E) composite in Figure 2 (b) indicates better compatibility among the PVA-SiO_2 with clay. From Figure 2(c) and (d), PVA-SiO_2-clay composites are dispersed unevenly with the presence of agglomeration due to high surface energy and poor adhesion between clay and PVA-SiO_2 matrix. They also show the poor compatibility of PVA-SiO_2 matrix with clay as the inert surface of PVA-SiO_2 cannot react well with the clay particles [19]. The clay (1.34TCN) composite shows the copolymerization of the PVA-SiO_2 with clay. However the dispersion of silica or clay is non-uniform in the composite film. The strong interfacial bonding between PVA-SiO_2 and clay (1.28E) shows higher mechanical and thermal properties compare to PVA-SiO_2-clay (1.30E) composite, PVA-SiO_2-clay (1.31PS) composite and PVA-SiO_2-clay (1.34 TCN) composite, respectively.

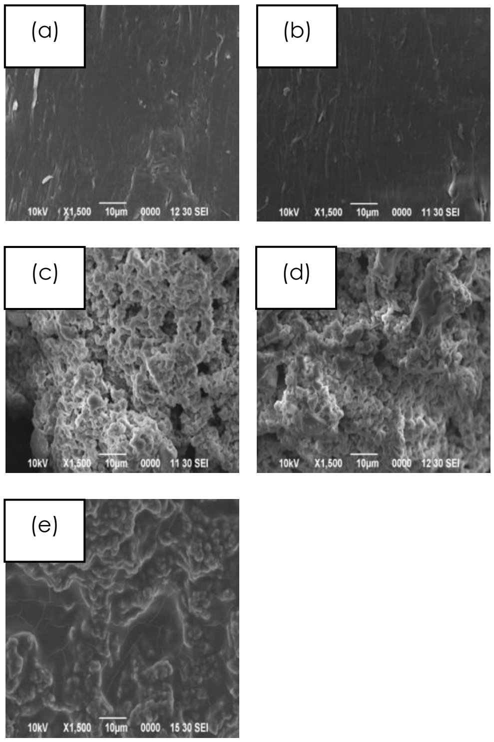


Figure 2 SEM micrographs of (a) PVA, (b) PVA-SiO_2-clay (1.28E) composite, (c) PVA-SiO_2-clay (1.30E) composite, (d) PVA-SiO_2-clay (1.31PS) composite and (e) PVA-SiO_2-clay (1.34TCN) composite

3.4 Adsorption Isotherm

The N_2 adsorption isotherms measure for PVA and PVA-SiO_2-clay composites is shown in Figure 3. For specific surface area, S_{BET}, it is calculated by the Brunauer-Emmett-Teller (BET) equation [20]. The surface areas for the pure PVA and PVA-SiO_2-clay (1.28E) composite, PVA-SiO_2-clay (1.30E) composite, PVA-SiO_2-clay (1.31PS) composite and PVA-SiO_2-clay (1.34TCN) composite are found to be 1.93, 11.16, 8.26, 6.05, and 8.86 m^2/g, respectively, which indicate an increase the surface area of composites compare to pure PVA. Due to the good dispersion of the clay within the PVA-SiO_2 matrix, the pores are decreased and enhance their accessibility for nitrogen adsorption. The isotherm patterns show the presence of a hysteresis loop, which is a characteristic feature of the type IV isotherms according to the original IUPAC classification [21]. In the case of PVA sample, the isotherm initially shows an initial ascending section up to $P/P_o=0.0017$, afterwards it shows a rather straight section, which extends up to $P/P_o=0.668$. Finally, the isotherm exhibits an upward sweep near saturation pressure. Similar pattern of isotherm is observed in the composites of PVA-SiO_2-clay (1.28E), (1.30E), (1.31PS) and (1.34TCN), with the initial ascending section extends up to $P/P_o=0.018$, 0.001, 0.001 and 0.013, respectively. The enhancement in the N_2 adsorption at high P/P_o values is observed for PVA-SiO_2-clay (1.28E) composite. After the incorporation of clay into PVA-SiO_2 matrixes, BET surface area and pore volume of PVA-SiO_2-clay (1.28E) and (1.34TCN) composites greatly increase, while the pore size decrease as shown in Table 3 [22]. The adsorption isotherms indicate that the pores are mesoporous. It proves that PVA-SiO_2-clay (1.28E) composite has the highest surface area and average pore volume with less pore size, which is reflected in the surface morphology.

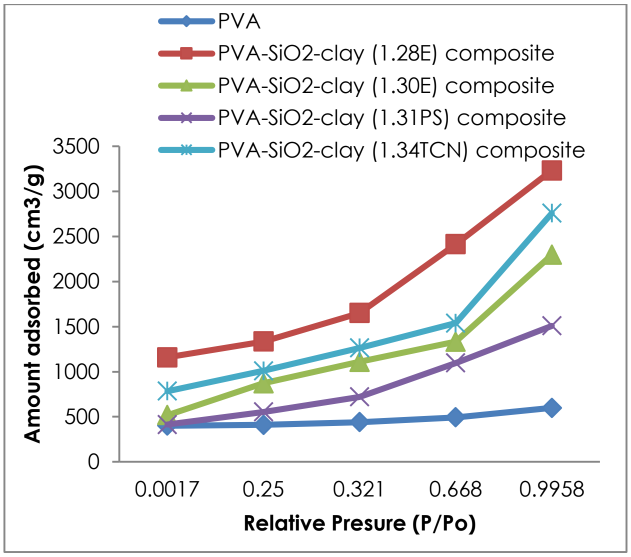


Figure 3 N_2 adsorption isotherms of PVA and PVA-SiO_2-clay composites

Table 3 Physical properties detected from N_2 adsorption at 77K on PVA and PVA-SiO_2-clay composites

Sample	Specific surface area, S_{BET}(m^2/g)	Average pore volume, V_m ($10^{-4}cm^3$/g)	d_{BET} (nm)	Type of Isotherms
PVA	1.93	0.00008	2.00	IV
PVA-SiO_2-clay (1.28E)	11.16	9.122	1.57	IV
PVA-SiO_2-clay (1.30E)	8.26	5.209	1.58	IV
PVA-SiO_2-clay (1.31PS)	6.05	4.060	1.58	IV
PVA-SiO_2-clay (1.34TCN)	8.86	8.361	1.57	IV

3.5 Tensile Properties

The tensile strength and tensile modulus of pure PVA and different types of clay loaded PVA-SiO_2 composites are shown in Figures 4 and 5 respectively. PVA-SiO_2-clay (1.28E) composite and PVA-SiO_2-clay (1.30E) composite have higher tensile strength compare to both pure PVA and other PVA-SiO_2-clay composites. It is shown that the tensile strength increases significantly when the clay is added to the PVA-si matrix [23]. The composites aggregate reduce inter-particle distance and therefore some silica is left unbounded to PVA.

According to Figure 5, PVA-SiO_2-clay (1.28E) composite have the highest tensile modulus compared to pure PVA and other PVA-SiO_2-clay systems. This is because the clay (1.28E) contained trimethyl stearyl ammonium, which imparted anti-wetting property and cause the surface of PVA-SiO_2-clay (1.28E) composite to become hydrophobic [24]. The addition of clay into PVA-SiO_2 (1.28E) system enhances the tensile strength and modulus and thus increases the compatibility between PVA-SiO_2 matrix and clay. The strong compatibility of PVA-SiO_2-clay (1.28E) composite is reflected in thermal properties and surface morphology.

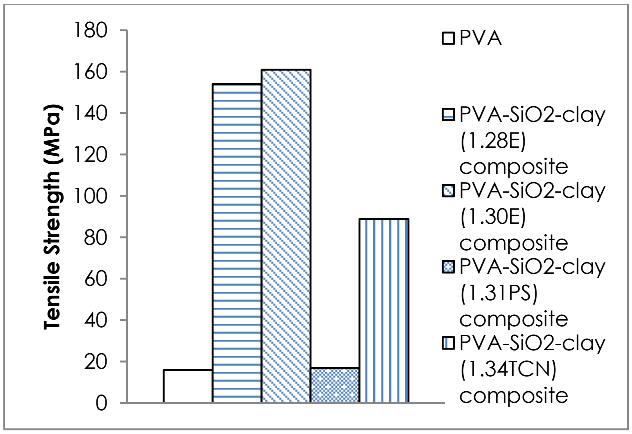


Figure 4 Tensile strength of PVA and PVA-SiO_2-clay composites

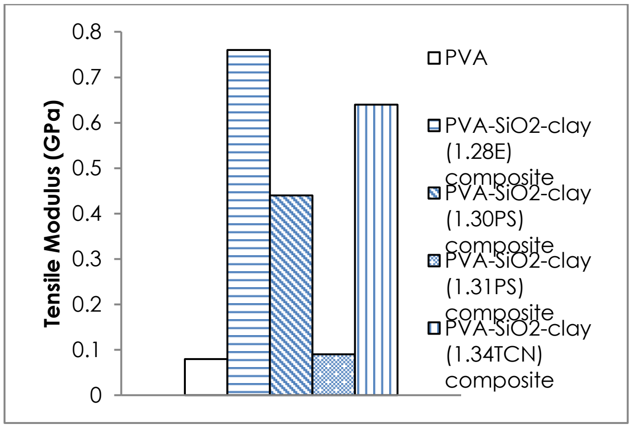


Figure 5 Tensile modulus of PVA and PVA-SiO_2-clay composites

3.6 Thermogravimetric Analysis (TGA)

Thermal stability is one of the most important parameters of polymer composites determining their suitability in actual applications. The thermal stability of pure PVA and PVA-SiO_2-clay composites are shown in Figure 6. It shows that thermal stability of different clay loaded composites significantly increase compared to the pure PVA alone. There are three steps in the thermal decomposition of PVA and composites. For the initial temperature of every step, it is defined as a critical point of weight loss for the sample in the TGA curve [25]. The first step is associated with the moisture loss or evaporation of trapped solvent. The second step is associated to the weight loss process corresponding to dehydration reaction on polymer chain, usually occurred from 250°C to 450°C [25]. The third step is associated with the polyvinyl alcohol residues degradation at about 450°C to produce carbon and hydrocarbon [16]. Different types of clay lead to different weight loss as there is a restriction in polymer chain mobility and suppression of decomposition. The clay and silica are well intercalated with polymer matrix by covalent bonds. The presence of silica particles along with clay in the polymer chain prevents complete decomposition of PVA-SiO_2-clay composites main chain [16].

According to the TGA thermographs, the first step degradation is occurred 85°C for pure PVA and different clay loaded composites. The weight loss is about 16%, 5%, 5%, and 8% for pure PVA, PVA-SiO_2-clay (1.28E), PVA-SiO_2-clay (1.30E), PVA-SiO_2-clay (1.31PS) and PVA-SiO_2-clay (1.34TCN) clay loaded composites, respectively. Different weight losses are visible due to the removal of moisture. The second step degradation occurs at 85°C to 250°C. The weight loss is found to be 10% for PVA and 7% for PVA-SiO_2-clay composites. It is indicated that the composites are more thermally stable compare to pure PVA due to the silica and clay loading. The final degradation temperature is 250°C to 430°C and weight loss is 8%, 1.5% and 1.3% for PVA, 1.28E composite and PVA-SiO_2-clay (1.30E, 1.31PS, 1.34TCN) composites, respectively. The final weight of composites is drastically less than pure PVA as the degradation temperature of silica itself is 360°C. The bonding compatibility of PVA-SiO_2 and 1.28E clay is higher than 1.30E, 1.31PS, 1.34TCN clay composites that is proven by tensile strength and modulus.

The activation energy can be helpful in reaching conclusions about the thermal stability of PVA-SiO_2-clay composites. The Arrhenius equation is used to determine the activation energy, which is summarized in Table 4. It is found that the activation energy of PVA-SiO_2-clay composites is significantly higher than that of pure PVA. The higher activation energy implies higher thermal stability.

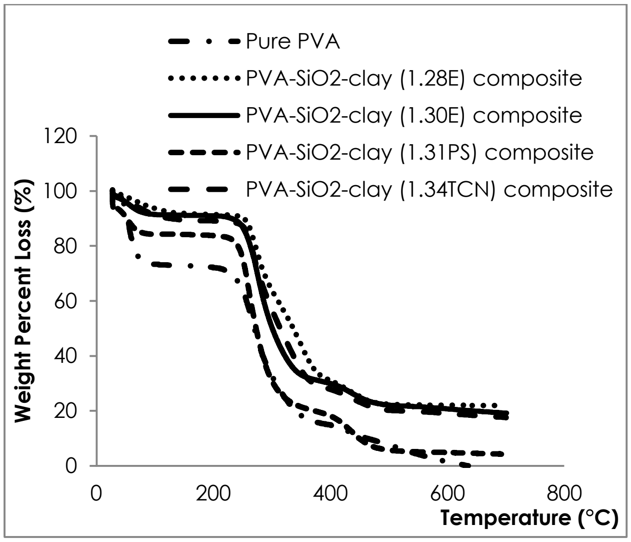


Figure 6 TGA curves of PVA and PVA-SiO_2-clay composites

Table 4 Activation energy of PVA and PVA-SiO_2-clay composites

Sample	T_i(°C)^a	T_m(°C)^b	T_f(°C)^c	W_{Ti}(%	W_{Tm}(°	W_{Tf}(°C)^f	Activation Energy, E_a(kJ/mol)
PVA	217	260	283	71	57	41	18
PVA-SiO_2-clay (1.28E)	267	300	350	79	57	35	40
PVA-SiO_2-clay (1.30E)	266	289	319	85	70	57	29
PVA-SiO_2-clay (1.31PS)	242	269	291	93	75	56	31
PVA-SiO_2-clay (1.34TCN)	240	264	285	81	62	41	40

[a] Temperature corresponding to the maximum rate of mass loss
[b] Temperature corresponding to the beginning of decomposition
[c] Temperature corresponding to the end of decomposition
[d] Mass loss at temperature corresponding to the maximum rate of mass loss
[e] Mass loss at temperature corresponding to the beginning of decomposition
[f] Mass loss at temperature corresponding to the end of decomposition

4.0 CONCLUSION

In this study, PVA-SiO_2-clay composites were prepared via solution intercalation method. The reduction of hydroxyl group and the dispersion of clay were confirmed by FT-IR spectroscopy. The FT-IR result successfully proved that polyvinyl alcohol and clay are compatible with silica and had altered PVA chains tri-dimensional structure. PVA-SiO_2-clay composites contain high percentage of S and K group which proved the presence of Si-O-Si stretching vibration and the clay mineral content respectively. SEM showed that strong interfacial bonding was formed between PVA-SiO_2 and clay (1.28E). BET results proved that PVA-SiO_2-clay (1.28E) composite had the highest surface area and average pore volume with less pore size. PVA-SiO_2-clay (1.28E) composite showed higher tensile strength and modulus compared to pure PVA, PVA-SiO_2-clay (1.30E) composite, PVA-SiO_2-clay (1.31PS) composite and PVA-SiO_2-clay (1.34TCN) composite. The bonding compatibility of PVA-SiO_2 and clay (1.28E) was higher than clay (1.30E, 1.31PS, 1.34TCN) composites, respectively. PVA-SiO_2-clay composites showed higher thermal stability and activation energy compared to the pure PVA. PVA-SiO_2-clay composites are biodegradable, environmental friendly and less cost on the production of the composites. These composites can be applied in biomedical devices such as coating surface on small artery replacement as well as functioned as an absorption membrane. Due to the limitation of the practical applications of PVA-SiO_2-clay composites, the future perspective is to produce the composites and applies them on the biomedical devices.

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