

Mechanical and Thermal Properties of Nanocomposite Films Made of Polyvinyl Alcohol/Nanofiber Cellulose and Nanosilicon Dioxide using Ultrasonic Method

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Abstract

Cellulose Nano fibrils have strong reinforcing properties when incorporated in a compatible polymer matrix. The aim of this study was to investigate the thermal and mechanical properties of the nanocomposite Nano composite made of poly vinyl alcohol (PVA)- Nano fiber celluloses (NFC)-Nano silicon dioxide Samples of the nanocomposite Nano composite were prepared by the casting method with different Nano cellulose and Nano silicon dioxide loadings. Then, samples were exposed to tensile test, Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The morphology of both neat poly (vinyl alcohol) and Nano composites was explored by using the field emission Scanning Electron Microscope technique (SEM). Results of tensile test indicated that the tensile strength and Young's modulus of poly (vinyl alcohol) composite Nano composite were significantly improved with the increase of cellulose Nano fibrils loading. Also, the Ultimate strength (UTS) decreased as the SiO₂ contents increased. The addition of 5 and 10 wt% of Nano silicon dioxide successfully improved the thermal stability and crystallinity of the PVA/Nano cellulose composites. Results indicated that the Nano cellulose had a great potential to reinforce PVA polymers.

Keywords: Polyvinyl alcohol, Nanofibercellulose, Nano silicon dioxide, Mechanical properties, Thermal properties.

1. INTRODUCTION

In recent years, there has been an increasing interest in fabricating of "bio composite" derived from natural resources in the academic and industrial areas of research [1]. Much more effort has been made to replace petroleum-derived polymers with natural, sustainable bio polymers because they are biodegradable, environmentally friendly and renewable with lower energy consumption [2].

Biodegradable composites have been a subject of interest for many years because of their potential to protect the environment by reducing non-biodegradable synthetic plastic waste.

Biodegradable composites are considered as a possible solution for environmental problems. The omission of some materials can be biodegraded to minimize the pollution. These materials not only provide the convenience for daily life but also minimize the impact on the environment after being used. In the long run, these materials into small environmentally friendly molecules be handled in properly controlled environment. Blends of Cellulose with synthetic polymers (e.g. polyvinyl alcohol, aliphatic polyesters, etc.) are prepared to achieve the desired performance for different applications [3].

The thermal resistance is one of the most dominative properties for polymer materials, as it ultimately governs the mechanical properties, durability, spectral stability, shelf lives, and life cycles of polymers.

By adding inorganic Nano-fillers to composite, thermal resistance of composite hosts is dramatically improved [6]. Fibers with higher hemicellulose content tend to absorb more moisture and char formation is generally better with fibers that have higher lignin content as they experience degradation at relatively lower temperatures [3,5]. For the purposes of reinforcement, cellulose is extracted from the natural fibers and used for the production of composites due to its hierarchical structure and semi crystalline nature [5]. Compared to virgin composite, polymeric/inorganic nanocomposites are usually significantly degraded at higher temperatures [5], indicating a substantial decrease in the degradation rate [8]. Hence, the thermal resistance of composite hosts can be markedly enhanced, even if only a small amount of nano-fillers is loaded [9]. Poly (vinyl alcohol) (PVA) is used as Biodegradable polymer due to their good chemical and physical properties like water solubility, chemical resistance, high melting point and biological compatibility. In addition, it is an inexpensive, non-toxic material, having high tensile strength and flexibility offering the possibility of functionalization due to its pendant hydroxyl groups. Cellulose is a renewable, biodegradable and the most abundantly available natural polymer in the world. The cellulose chains are associated to one another by hydrogen bonding between hydroxyl groups. This interlinking results in high stiffness and structural strength to the material [3]. High mechanical strength, lightweight, high length-to-diameter ratio, and large specific surface area are a few of omitting the well-known characteristics of Nano cellulose [11]. In the current study, the environmentally-friendly Nanocellulose -based polymer composite Nano

composite with enhanced mechanical, and thermal properties were produced. More specifically, the aim of present study was to investigate the effect of the concentration of cellulose Nano fibrils and Nano silicon dioxide on the morphological, mechanical, thermal gravimetric analysis of PVA Nano composite.

Initially, field emission scanning electron microscopy (SEM) were conducted to investigate the surface morphology of the PVA/NFC Nano composite. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were also carried out in order to determine the thermal properties of the examined material. Finally, the mechanical properties of the Nano composite were studied through the evaluation of their tensile strength and elongation at break.

2. EXPERIMENTAL

2.1. Materials

Polyvinyl alcohol (PVA) (average molecular weight: 72000 g/mol; polymerization degree: 1600; hydrolysis degree: 97.5 – 99.5 mol %), was purchased from Sigma Aldrich in Germany. Nano fiber cellulose Bleached softwood Kraft pulp was supplied by SCA's pulp mill (Östrand, Sweden) and Nano silicon dioxide ,10-20 nm particle size, 99.5% trace metals basis by Sigma-Aldrich (Germany).

2.2. Synthesis of PVA and Nanocellulose Fiber/ Nano Silicon Dioxide Films Nanocomposites

PVA and NFC-reinforced PVA composite Nano composite were prepared using a solvent casting method. Five grams of PVA were dissolved in 100 mL of distilled water at 90 °C for 60 min under mechanical stirring. Then, the solutions were kept under stirring to reach room temperature. The dissolved solution was cast on Teflon glass plate (10×10 cm) and slowly dried at room temperature for 24 h. The resultant film was peeled from the casting surface. To obtain Nano composite

Nano composite, the NFC solutions and silicon dioxide Nano-powder were mixed with the previously prepared PVA solution and sonicated for 30 min at room temperature using a sonicator (Misonix Inc., model S-4000). The resulting mixture was cast in a Teflon glass plate (petri dish) and placed in an oven set at 35 °C to evaporate water. Composite Nano composite with different NFC loadings (5, 10 and 20 wt %) were prepared. The obtained Nano composite were conditioned at 23 ± 2 °C and $50 \pm 5\%$ relative humidity for at least 48 h prior to testing. Table 1 shows the composition (% wt) of the materials in each sample type.

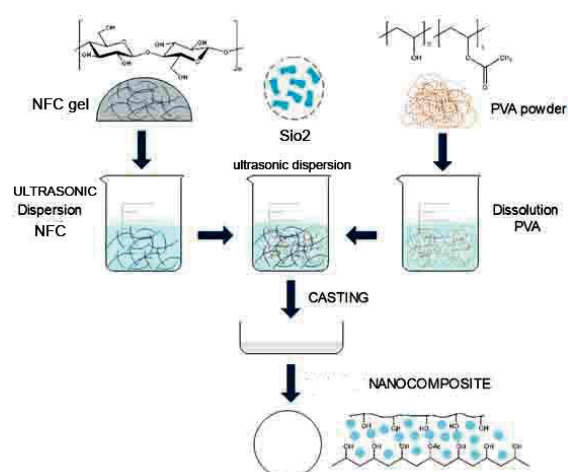


Figure.1. Synthesis of PVA and Nano cellulose fiber/ Nano silicon dioxide films nanocomposites.

Table 1. Composition of the materials in each Nano composite sample type.

Nanocomposites	PVA	Nanofiber Cellulose (NFC)	Nanosilicon dioxide (SiO ₂)
PVA	100	0	0
PVA/NFC 1	90	10	0
PVA/NFC 2	80	20	0
PVA/S 1	90	0	10
PVA/S 2	80	0	20
PVA/NFC/S 1	90	5	5
PVA/NFC/S 2	80	10	10

2.3. Characterization

2.3.1. Water Vapor Permeability (WVP)

The Water vapor permeability methodology described in the ASTM E96 were used to measure the WVP of the film. Due to weight changes over time, the water vapor transmission rate through the film (the amount of WVP) was calculated.

2.3.2. Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g), cold crystallization (T_c) and melting temperature (T_m) of the samples were determined by DSC measurements, using a differential scanning calorimeter. Nine Nano composites were scanned at a rate of 10 °C/min from 25 to 400 °C, under nitrogen atmosphere and at a flow rate of 20 mL/min). The scanning process involved an initial heating followed by cooling, and finally second temperature scan [5].

2.3.3. Thermo Gravimetric Analysis (TGA)

Thermal behaviour of the prepared samples were examined by Thermo gravimetric Analyzer model (TA Instruments, Model Q500) from 20°C to 400°C. A heating rate of 10°C/min was used under nitrogen atmosphere and at a flow rate of 20 mL/min. The weight change in relation to temperature and decomposition temperature was investigated as described. The weight change in relation to temperature and decomposition temperature (T_{dec}) was investigated by the same method as described [7].

2.3.4. Scanning Electron Microscopy (SEM)

SEM was performed to investigate the surface and cross sectional morphology of the PVA/CNF/SiO₂ composite membranes with varying proportions of Nano cellulose. FE-SEM micrographs of the surfaces of specimen were taken using FE-SEM model TESCAN MIRA 3 XMU was used with an acceleration voltage of 5 kV.

2.3.5. Mechanical Properties

The mechanical behavior (tensile Modulus % elongation at break (% Eb) and elastic modulus) of the various PVA/Nano cellulose / Nano silicon dioxide composite membranes with varying proportion of Nano cellulose and Nano silicon dioxide was determined using a universal testing machine (Model TVT-3800, Instron TEXVOL SWE) tensile testing equipment. Five specimens were tested at 25°C. The test was carried out in accordance with the standard test method ASTM D882. The dimensions of the test specimens were: length 50 mm, width 8 mm and thickness 0.1 mm. The cross head speed used was 50 mm/min.

3. RESULTS AND DISCUSSION

3.1. Water Vapor Permeability

As shown in (Figure 2), test results of the apparatus and methodology described in the ASTM E96 were used to measure the W_{VP} of the film. W_{VP} is one of the important properties of film polymers, especially bio polymers. The presence of moisture and water vapor is the one of the main reasons for the reactions in spoilage. Polymers permeability is directly affected by hydrophilic or hydrophobic nature of compounds, process and production of polymer, polymer type and amount of additives, presence of pores and cracks, and the polymer structure. Adding nanoparticles to the matrix reduces the penetration of water vapor molecules and provides a winding route for the passage of water molecules by increasing the coherence between the chains and decreasing pores (empty spaces). In addition, it decreases the rate of penetration and thus reduces the W_{VP} .

However, the results of this study showed that with increasing Nano silicon dioxide the sample had the lowest W_{VP} as shown in (Table 2). The lowest W_{VP} in 10% Nano silicon dioxide and 10% Nano cellulose sample might be due to the relatively strong interactions between the

matrix and filler in the film containing Nano particle.

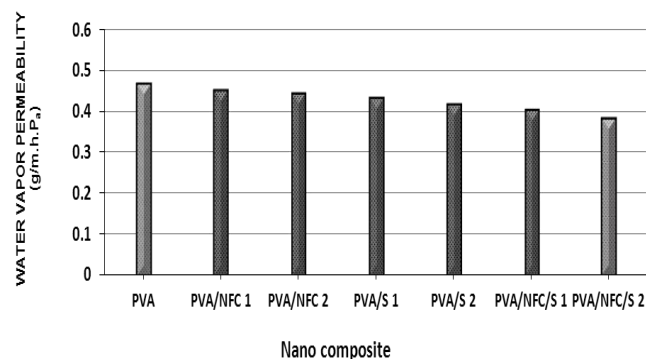


Figure 2. Water vapor permeability of PVA Nano composites.

Table 2. Water vapor permeability test results and effect of adding Nano particles.

Sample type/ Nano particle content	Water vapor permeability (g.m.h.P _a)
PVA	0.4685 ± 0.59
PVA/NFC 1	0.4512 ± 0.15
PVA/NFC 2	0.4437 ± 0.07
PVA/S 1	0.4325 ± 0.14
PVA/S 2	0.4175 ± 0.11
PVA/NFC/S 1	0.4048 ± 0.04
PVA/NFC/S 2	0.3822 ± 0.02

It could be also concluded the blending of Nano silicon dioxide with thermoplastic PVA modified the W_{VP} properties, and these changes were strongly associated with the dispersion of Nano silicon dioxide in the polymer matrix. In fact, the reasons for this conclusion could be attributed to existence of more coherent structure with high cohesion and free space in the polymer that is filled due to the addition of nanoparticles. On the other hand, oxide silicon fillers were less hydrophilic than the matrix resulting in the reduction of permeability of the Nano composite.

3.2. Differential Scanning Calorimetry (DSC)

(Figure 3) shows the thermal properties of PVA with Nano cellulose and Nano silicon dioxide. DSC is performed to study

the glass transition (T_g) temperatures, crystallization temperatures (T_c) and melting temperatures (T_m) of the nanocomposite. Figure 2 shows the DSC curves of all formulated Nano composite. The first heating cycle removes any thermal history and moisture of the PVA composite systems [6]. As seen in (Figure 3), all samples showed initial weight loss at about 70–100 °C, which might be due to the result of water evaporation. It is quite apparent that nanocomposite the crystallization temperature was increased with the addition of Nano cellulose and Nano silicon. The weight loss was in the range of 5wt% except of the 10 wt% Nano cellulose loading. According to the curves, major degradation temperature was occurred between 280 °C and 350 °C as shown in (Figure 3). The degradation temperature of the nanocomposites increased as the Nano cellulose content increased, and the major degradation peak temperature was shifted to higher temperature. The effects of 10 and 20 wt% of Nano cellulose loadings on the thermal properties were observed. Table 1 shows DSC thermo grams test results and the effects of adding Nano cellulose and Nano Silicon dioxide of nanocomposites Nano composite with different weight ratios. The thermal stability of the nanocomposite increased above these loading levels of Nano cellulose and Nano oxide silicon especially at the 5wt% loading. The thermal stability of the PVA/Nano cellulose composites increased with the addition of small amounts of Nano silicon dioxide. This result proved that the thermal properties of Nano cellulose -reinforced PVA could be improved with a low Nano silicon dioxide content, possibly due to the high thermal stability behavior of Nano silicon dioxide. Thus, thermal stability of PVA/Nano cellulose was induced by the reinforcement of small amounts of Nano silicon dioxide [6]. This result also indicated that the well-dispersed Nano silicon dioxide particles successfully acted

as effective nucleation agents in the PVA/Nano cellulose composite.

Table 3. Summary of DSC test results and effect of adding Nano cellulose and Nano Silicon dioxide of Nano composites with different weight ratios.

Nano composites	T_g	T_c	T_m
PVA	88	310	371
PVA/NFC 1	113	322	373
PVA/NFC 2	118	323	378
PVA/S 1	123	325	380
PVA/S 2	125	326	383
PVA/NFC/S 1	126	328	385
PVA/NFC/S 2	128	329	387

as shown in (Table 3), the thermo gravimetric analysis (DSC) was used to study the effects of Nano cellulose and Nano Sio₂ on the thermal stability of the composites. The resulting DSC curves of neat PVA film, PVA/NFC/ Nano silicon dioxide are showed in (Figure 3). DSC curves indicate the maximum decomposition temperature. Then, T_g value was increased with increasing PVA /NFC/ Nano silicon dioxide content for the blend sample 10/10 wt%. Differences in shape and area of the melting endotherm are also noticed. The melting point is a physical parameter used to identify the nature of the substance and its degree of purity. As seen in table 2, the melting points (T_m) for the blend samples were more than value of PVA.

3.3. Thermo Gravimetric Analysis (TGA)

TGA curves of different Nano composite are exhibited in Figure 4. The thermal degradation process, corresponding decomposition temperatures and weight loss of each Nano composite were observed. From Figure (4.c), the PVA/NFC/s 2 and PVA/NFC/s 1 presented higher thermal stability, especially in the temperature range between 300 and 400 ° C.

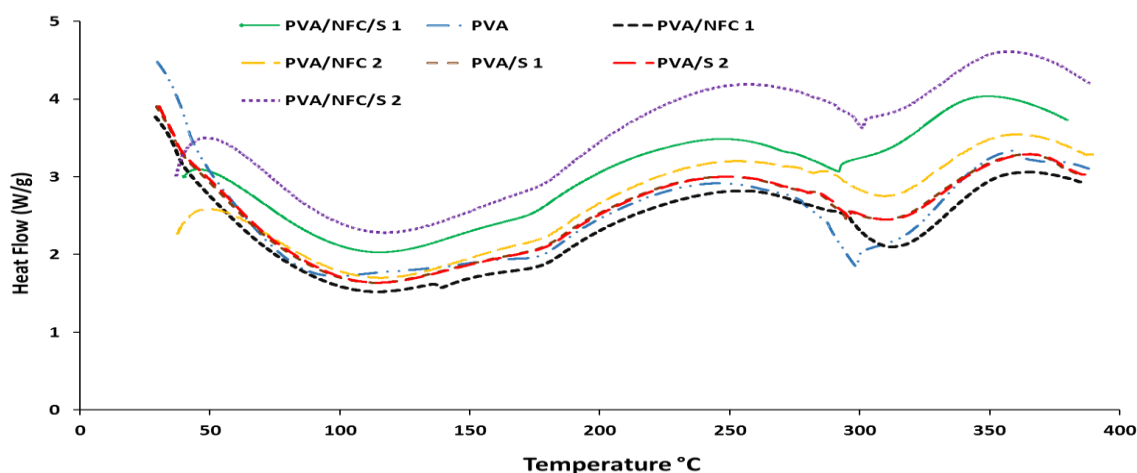


Figure 3. DSC curves for Nano composite with various amounts of Nano particles.

As can be seen from Figure (4.c), compared to other Nano composites, the PVA/NFC/S 2 and PVA/NFC/s 1 also exhibited better thermal stability, especially in the temperature range between 200 and 300 ° C. From Figures 4 the TGA curves of seven kinds of Nano composite, it can be seen that their mass loss can be divided into three stages. The first stage was attributed to the volatilization of water adsorbed in the composites before 100 ° C, and the second stage started at about 250 ° C. This was caused by the absorbed moisture and the degradation of the side chains of PVA molecules. And the third stage began at about 350 ° C, which was resulted from the degradation of the main chains of PVA molecules and the combustion of carbon materials [7]. In addition, PVA/CNF/S Nano composite membranes presented the lowest degradation degree compared to other Nano composites. After making a comparison between Figure 4a, 4b and 4c, it can be seen that the modification of Nano silicon dioxide can improve the thermal stability of PVA between 100 and 300 °C. However, the thermal stability was decreased when the temperature was higher than 300 C. The thermal behavior of the sample PVA/NFC 2 (Figure 4. a) was very similar to the sample PVA/NFC 1. The film PVA/S 1 started to lose weight at a temperature of about 80 ° C and

continued up to a temperature of 150 °C, associated with the release of moisture. Another drop was observed in the temperature range 250–350 °C, which caused the film to lose weight. Another drop was found in n the temperature range 300–400 °C. In the end, of the film remained solid. (Figure 4. b) shows a film similar to in Nano composite containing 80% polyvinyl alcohol and 20% Nano silicon. The film contains 90% polyvinyl alcohol with 5% Nano cellulose and 5% Nano silicon in the temperature range 200 to 300 degrees more than other Nano composite, but after a temperature of 300 ° C to 400 more resistance to heat in the film. (Figure 4.C) shown a film PVA/NFC/S 2 in the temperature range 100-150° C with a 2% drop, but after a temperature of 200 ° C to 350 ° C a drop of intense relative to the heat seen in the film. Finally, at a temperature of 400 ° C, maximum of the solid remained.

3.4. Mechanical Properties

As seen in (Figure.5), the results of tensile strength test, showed the stress-strain curves of the samples. PVA showed a typical curve having a yield point. The elongation at break was dramatically decreased by the addition of Nano silicon dioxide to PVA. While the elongation at break of PVA/S 2 composites was lower compared to PVA.

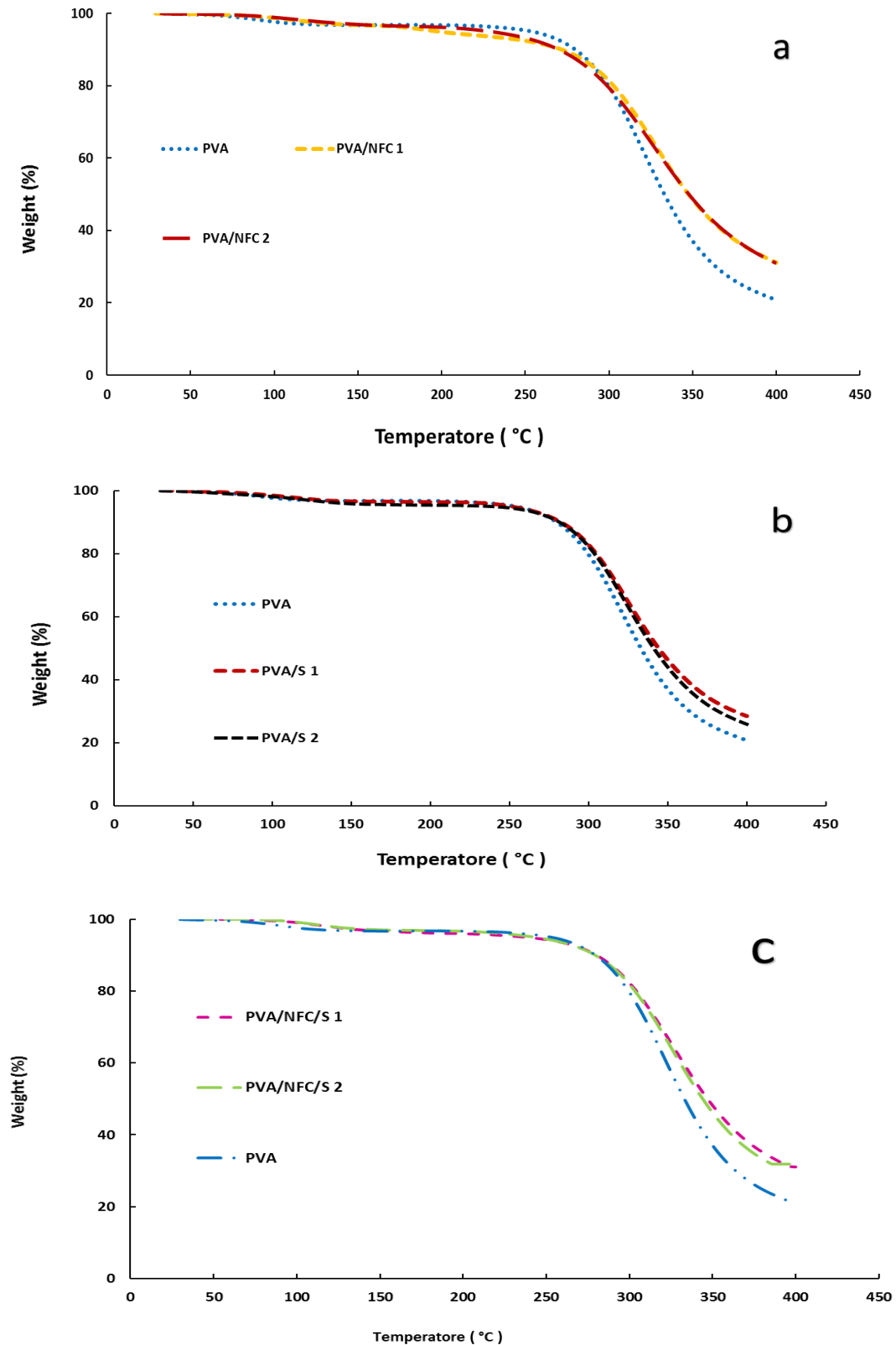


Figure 4. Results of thermograms (TGA) Nanocomposites with various amounts of Nanoparticles and its effect. (A) PVA and NFC % (B) PVA and SiO_2 % (C) PVA and NFC and SiO_2 .

The entire Young's modulus of the composites was increased with increasing Nano silicon dioxide spherical particle is a rigid part in the Nano composites and Nano fiber celluloses can bond with PVA by the hydrogen bond.

The tensile strength of neat PVA film was 3.88 MPa. As the loading of NFC increased from 5, 10, 15 and 20 wt% (based on PVA weight), tensile strength of PVA composite Nano composite increased from 4.39 to 4.69 and 4.52, 3.96; respectively.

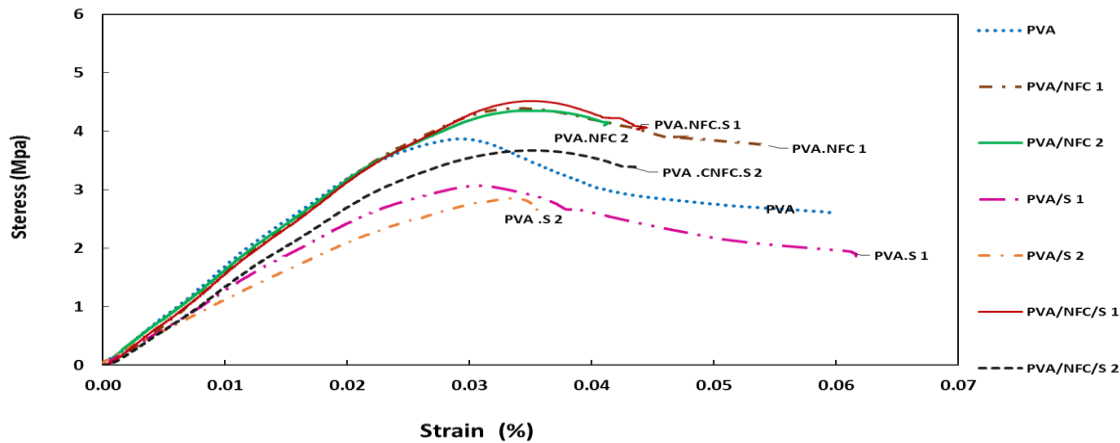


Figure 5. The stress-strain curves, PVA composites with various contents of Nano particles.

(Figure 6) shows the results of tensile strength test on neat PVA and PVA/NFC/S nanocomposites. The tensile strength of neat PVA film was 3.87 MPa. As the loading of CNF increased from 5 to 10 wt%, tensile strength of Nano composite Nano composite increased.

The intermolecular forces keep the inherent tensile strength of the fibrils intact and results in enhancement of the tensile strength of the Nano composite [5]. It is worth noting that the mutual affinity of the PVA matrix and NFC with hydroxyl-rich surfaces, leads to the strong interactions between them [9]. The resulting hydrogen bonds should strengthen the interface significantly with a positive impact on the mechanical properties of the composite material. Therefore, these interactions can partially hinder the formation of the expected percolating cellulosic network [1]. The TS of Nano composite could be increased significantly with the increase of NFC content as reported [6]. This could be due to high molecular weight and tight fittings of NFC compared to PVA.

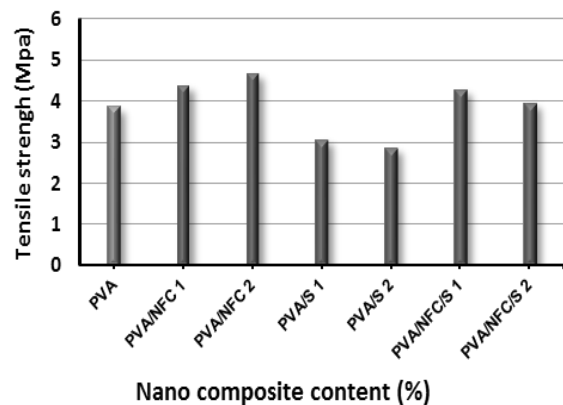


Figure 6. Mechanical properties of PVA/NFC/SiO₂ Nano composite Tensile strength.

Therefore, the addition of Silicon dioxide 5% to the PVA/NFC polymer matrix could largely affect the polymer's flexibility with only variations of a small change in tensile strength [3]. The TS showed the highest value when 5 wt % of SiO₂ was added into PVA/5 wt% Nano cellulose 5 wt% Nano silicon dioxide. The elongation at break of highest are shown in (Table. 4).The nanocomposites with 10, 20 wt% NFC and 10, 20 wt% Nano silicon dioxide showed an elongation at break of the least amount.

This may be due to the rigidity of matrix increased by adding the Nano particle [10]. Moreover, strong interaction between cellulose Nano fibrils and PVA could restrict chain movements and consequently blocks its ability to flow and reduce its ductility [8].

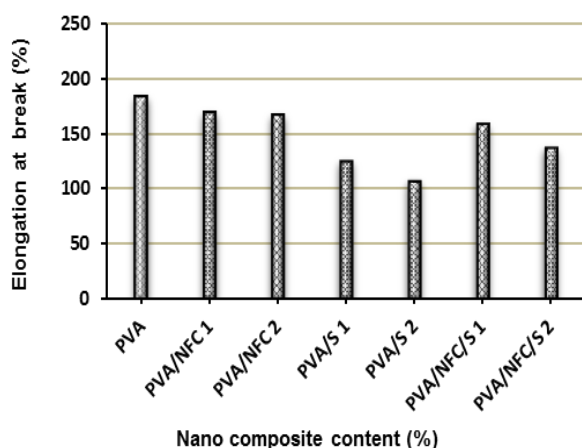


Figure 7. Mechanical properties of Nano composite elongation at break.

Table. 4. Summary of tensile strength and elongation at break results.

Nano composite	Tensile strength (Mpa)	elongation at break (%)
PVA	3.88	183
PVA/NFC 1	4.39	166
PVA/NFC 2	4.69	168
PVA/S 1	3.06	124
PVA/S 2	2.85	107
PVA/NFC/S 1	4.27	158
PVA/NFC/S 2	3.95	136

Figure 7 shows the effects of cellulose Nano fibrils on the elongation at break of Nano composite Nano composite. As can be seen, the percentage of elongation at break decreased with increasing of cellulose Nano fibrils concentration. PVA showed an elongation at break of 183 %, whereas the nanocomposites with 5, 10, NFC and 5, 10, wt% Nano oxide Silicon showed an elongation at break of 168%, 166%, 124% ,107 % ,158%, and 136% respectively.

This is because the rigidity of matrix increased by adding the NFC and Nano dioxide silicon [14]. Moreover, strong interaction between cellulose Nano fibrils and PVA chains could restrict chain movements and consequently blocks its ability to flow and reduce its ductility [10,14].

3.5. Morphology of Nano Composite

Microphotographs of nanocomposite are shown in Figure 8 (a and f). Voids signifying cellulose Nano fibrils pull-outs were observed for composites with NFC content up to 20% and 10 %. The images showed that fracture surface was relatively rougher for the Nano composites compared to the neat PVA Nano composite (Figure.8. a). Generally, the images showed that the cellulose Nano fibrils were homogeneously dispersed in the PVA matrix. The white dots (Figure 8 (d and e), having different sizes, on the Nano composites, can be considered as Nano silicon dioxide. The amount of these smaller white dots was increased with increasing Nano silicon dioxide content, indicating that these smaller white dots were mostly indications of Nano silicon dioxide dispersed in PVA matrix. Furthermore, the processing route used, which involved sonication followed by solution-casting, can be considered as an efficient method to distribute cellulose Nano fibrils reinforcements in PVA matrix.

4. Conclusions

The effect of Nano silica on the mechanical and thermal properties of PVA/Nano cellulose composites was investigated. The W_{VP} test, showed that Increasing Nano silicon dioxide by 10% and Nano cellulose by 10% in nanocomposites led to a significant decrease in the Nano composite' W_{VP} as a result the higher concentration of Nano silicon dioxide (10%) had a significant influence on the nanocomposites W_{VP} [4].

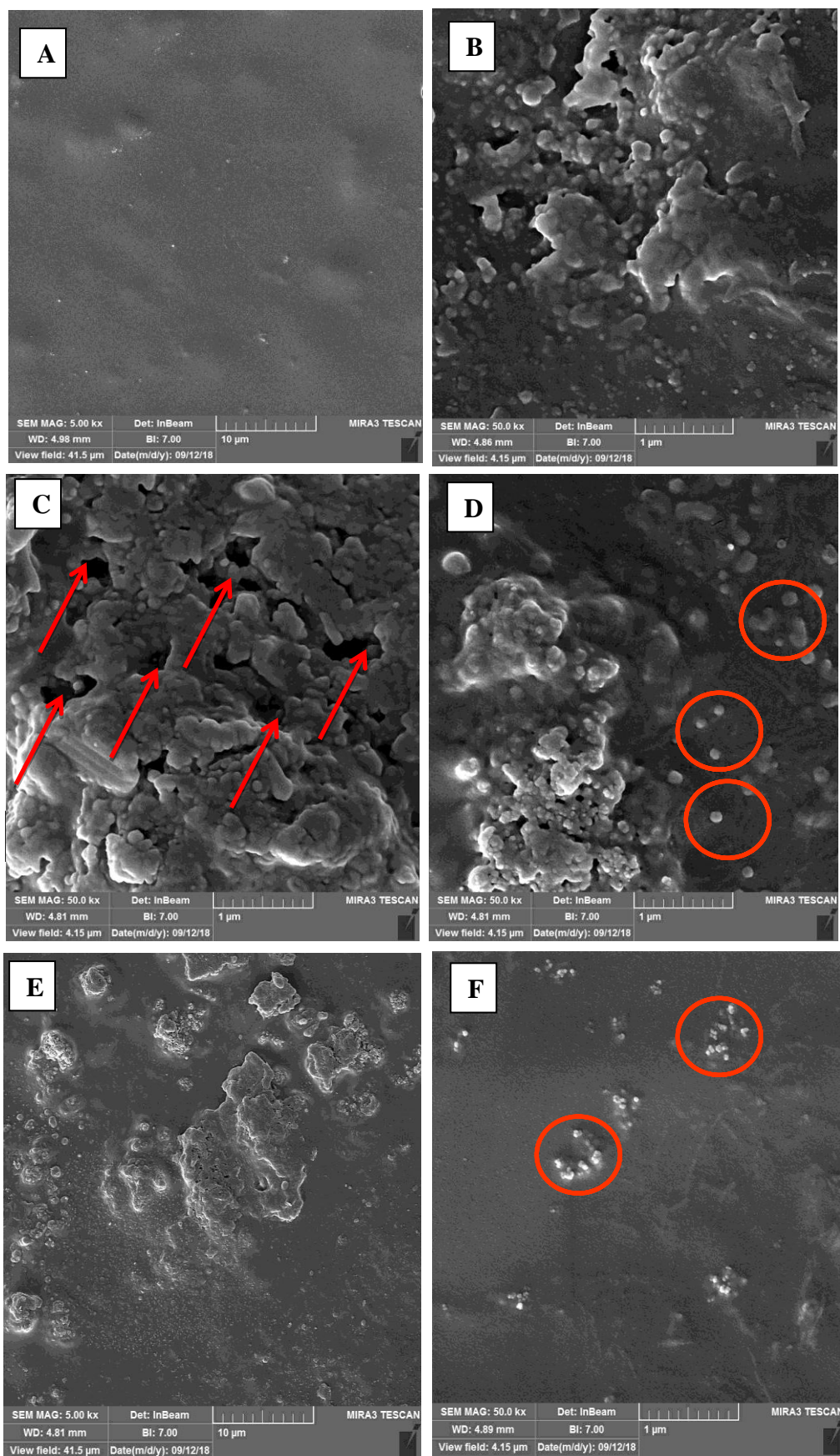


Figure 8. SEM micrographs of fracture surface of composite Nano composite: A) PVA; B) PVA/NFC2; C) PVA /NFC/S; D) PVA/S 1; E) PVA/ S2; F) PVA/NFC/

The thermal properties of Nano cellulose-reinforced PVA with low Nano silicon content are probably improved due to the high thermal stability behaviour of Nano silicon dioxide. The specific surface area of Nano -silicon dioxide also contributes to the greater interaction between the Nano-column and the PVA matrix, which leads to reinforcement and thermal stability. These results are consistent with the results of [11].

The tensile strength was increased in the nanocomposites with the addition of Nano cellulose content, the introduction of secondary reinforcement, and the restriction of mobility of the Nano composites due to the addition of Nano particles. Accompanied by a significant decrease in elongation at break. This result is consistent with the results of [11]. The highest tensile strength is related to the addition of 20% nanofiber cellulose to polyvinyl alcohol polymer, which increases the tensile strength compared to nanocomposites containing 10% nanofiber cellulose. This increase in tensile strength may be due to the inherent high tensile strength of Nano celluloses which acted as a suitable reinforcer and were able to form a good bond with the

polymer. The addition of 5 and 10 wt% of Nano silicon dioxide successfully improved the thermal stability and crystallinity of the composites. In this study, the nanomaterials-reinforced PVA composites containing 5 wt% of Nano cellulose and 5 wt% of Nano silicon dioxide significantly improved thermal and mechanical properties.

SEM results showed that NFC was uniformly distributed in the PVA matrix and improvement of structural properties could mainly be attributed to the presence of Nano silicon dioxide in Nano composite and the good interaction between the surface hydroxyl groups of Nano silicon dioxide and the functional groups of both polymers.

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