

Nanofibrillated Cellulose/Nano SiO₂/Poly(vinyl alcohol) Composite Films: Evaluation of Properties

Mohammad Ali Bay,^a Habibollah Khademi Eslam,^{a,*} Behzad Bazyar,^a Abdollah Najafi,^b and Amir Hooman Hemmasi^a

Effects of nanofibrillated cellulose (NFC) and nano-silicon dioxide on dynamic mechanical thermal analysis and physical properties of nanocomposites films made of poly (vinyl alcohol) (PVOH) were investigated. For this purpose, the nanoparticles were mixed with PVOH at 0%, 5%, and 10% weight. Water absorption, dynamic mechanical thermal, transparency, and wettability properties were evaluated according to corresponding standard test methods. The morphology of nanocomposites was explored by using a field emission scanning electron microscope technique. The films became increasingly opaque with increasing nanoparticles contents, although the composites also retained moderate transparency. According to the results of the tests, the dynamic mechanical thermal (DMTA) properties of PVOH composite films were significantly improved with the increase of NFC and silica nanoparticles loading. The samples containing 20 wt% of nano-SiO₂ exhibited higher hydrophobicity compared with that of 20 wt% NFC.

DOI: 10.15376/biores.17.1.1031-1046

Keywords: Poly vinyl alcohol; Cellulose Nano fiber; Nano silicon dioxide; Dynamic mechanical thermal analysis

Contact information: a: Department of Wood and Paper Science and Technology, Faculty of Natural Resources and Environment, Science and Research Branch, Islamic Azad University, Tehran, Iran; b: Department of Wood and Paper Science and Technology, Islamic Azad University, Chalous Branch, Chalous, Iran; *Corresponding author: hkhademieslam@gmail.com

INTRODUCTION

In recent years, increased environmental awareness and the fossil depletion problem have increased interest in biodegradable polymers. It is expected that the use of biodegradable biopolymers can solve some of the problems (Weber *et al.* 2002). The use of natural fibers as reinforcements in composites has attracted much attention due to environmental concerns. Natural fibers have received a lot of attention due to their renewable and highly available resources. Composites made of polymers as matrix and synthetic fibers or natural fibers as filler have shown increasing application due to their better properties. Due to serious environmental issues, they have been considered as an alternative to fillers and inorganic fibers (Chuah *et al.* 2006). The properties of natural fibers are closely related to the nature of cellulose and its crystallization properties. Among natural fibers, cellulose is the most abundant, most renewable, and degradable and biodegradable biopolymer in the world. Cellulose is made up of nano-sized microfibrils made up of crystalline and amorphous regions. Cellulose chains are laterally stabilized by hydrogen bonds between hydroxyl groups. Therefore, they have high structural strength and rigidity (Mandal and Chakrabarty 2014). The result of interconnection of cellulose

chains leads to high structural hardness and strength in the material and high mechanical strength, light weight, long length to diameter ratio, and high specific surface area are well-known features of nanocellulose (Niazi and Broekhuis 2015). Poly(vinyl alcohol) (PVOH) is a common and well-known polymer that has outstanding properties such as water solubility, film-forming properties, and biodegradability. Its global production is about 650,000 tons per year (Orts *et al.* 2005). PVOH is used as a degradable polymer due to its good chemical and physical properties such as chemical resistance, high melting point, and biological compatibility. In addition, it is an inexpensive and non-toxic material that has high tensile strength and flexibility. In addition, it has the potential to perform well due to its free hydroxyl groups. However, brittleness and low thermal stability, high flammability, medium gas barrier properties, and low solvent resistance against water of the neat PVOH are often insufficient for its applications.

The effects of nanoparticle SiO₂ (crystalline) on composite films and its use as an enzymatic immobilizer in food packaging as a shelf-life enhancer have been investigated (Ariyaratna *et al.* 2017). Nanofibrillated cellulose, as a reinforcer in various polymers, has been studied in recent years. In the case where the interfacial interaction is strong, the mechanical properties are increased, because applied stress can be effectively transferred from matrix to the fiber. The prepared nanocomposite increased tensile strength and elongation to failure compared to the pure polymer. However, increasing the percentage of nanocellulose to 10% tensile strength increased and then decreased tensile strength, as reported by (Zhang *et al.* 2012). These authors also studied several composites by preparing nanocomposites using polyvinyl fluoride and nanocrystalline cellulose and investigated its mechanical properties. The results of this study showed an increase in tensile strength and elongation to failure with an increasing percentage of nanocellulose. These properties increased with increasing nanocellulose up to 0.1% and then there was a decrease.

The water absorption by composite materials appears to involve three different mechanisms, which includes the diffusion of water molecules, capillary transport into the gaps and flaws, and the transport of micro-cracks in the matrix (Wu *et al.* 2011). Various factors such as the ratio of hydrophilic and hydrophobic groups, porosity, winding paths, and gaps in the film structure affect the degree of permeability of films to water. Nanoparticles can fill the space and intermolecular cavities between the matrix as fillers, thus reducing the intermolecular distances that form more compact films.

In this research, the effects of adding small amounts of NFC and also nano silicon dioxide (SiO₂) particles on physical properties of nanocomposites made of PVOH were investigated. For this purpose, appropriate tests including water absorption, transparency of composite films, and composite films with wettability were performed. Dynamic mechanical thermal analysis (DMTA) tests were also conducted in order to extract the glass transition temperature of films in order to study the thermal characteristics of nanoparticles. The results are presented, and the observations are reported in this paper.

EXPERIMENTAL

Composite and Sample Preparation

In this research polyvinyl alcohol (PVOH) with 72,000 gr/mol polymerization degree: 1600; hydrolysis degree: (97.5 to 99.5 mol %), and nanofibrillated cellulose from softwood kraft pulp was supplied by a pulp mill in Östrand, Sweden, and nano silicon dioxide (SiO₂), with 10 to 20 nm particle size and 99.5% trace metals basis, by Sigma-

Aldrich (Merck KGaA, Buchs, Germany) was used. These ingredients were mixed to make biodegradable nanocomposite.

Nanocomposite films were prepared using a solvent casting method. The specified amount of poly vinyl alcohol (PVOH) was dissolved in 100 mL of distilled water at 90 °C under agitation. The solutions were then stirred to reach ambient temperature. The solution was cast on a glass plate (10 × 10 cm) and slowly dried at room temperature for 24 h. The obtained nanocomposite films, the NFC suspensions, and the silicon dioxide nano-powder were mixed with the previously prepared PVOH solution and sonicated for 30 min at room temperature using a sonicator.

The resulting mixture was cast in a glass plate (petri dish) and placed in an oven set at 35 °C to evaporate water. Composite films with different nanoparticle loadings (5, 10, and 20 wt%) were prepared. Table 1 shows the composition (wt%) of the materials in each sample type. Table 1 shows the composition (wt%) of the materials in each composite sample (code name P0 to PFS2).

Table 1. Composition of the Materials in Each Nanocomposite Sample Type

| Specimen Code | PVOH wt% | Nanofibrillated Cellulose wt% | Nano- Silicon Dioxide wt% |
|------------------|----------|-------------------------------|---------------------------|
| P ₀ | 100 | 0 | 0 |
| PF ₁ | 90 | 10 | 0 |
| PF ₂ | 80 | 20 | 0 |
| PS ₁ | 90 | 0 | 10 |
| PS ₂ | 80 | 0 | 20 |
| PFS ₁ | 90 | 5 | 5 |
| PFS ₂ | 80 | 10 | 10 |

Methods

Water absorption tests were performed according to ASTM D7031-11 (2011). Dynamic mechanical thermal analysis (DMTA) was evaluated by ASTM D 4065. Film transparency was determined by ASTM D1746-09, and contact angle tests were conducted according to corresponding ASTM D7334 - 08(2013) standard test methods. In each case, the goal was to study the effects of adding the above-mentioned NFC and nano-SiO₂ and to determine the characteristics of the resulting nanocomposites. SEM micrographs of the surfaces of specimen were taken using FE-SEM model TESCAN MIRA 3 XMU, which was used with an acceleration voltage of 5 KV. The tests were repeated at least five times, and statistical analysis was performed.

RESULTS AND DISCUSSION

Water Absorption

Figure 1 shows the effect of the amount of cellulose nanofiber and nano-silicon oxide on the water absorption of nanocomposite films with different particle contents. Water absorption was performed according to ASTM D7031-11 (2011). Samples were first dried in an oven and their initial weight and dimensions were determined. Due to partial degradation and insufficient resistance, the adsorption of the samples after immersion in distilled water as well as their weight was measured after 2 hours.

In Fig. 1, results for the moisture absorption of nanocomposites with different nanoparticle contents are presented. Moisture absorption in a film depends primarily on the hydrophilicity of the polymer or biopolymer and then the presence of cavities and cavities between the chains. Due to the loss of samples, the moisture absorption of the samples after immersion in water was accurately measured in just 2 hours.

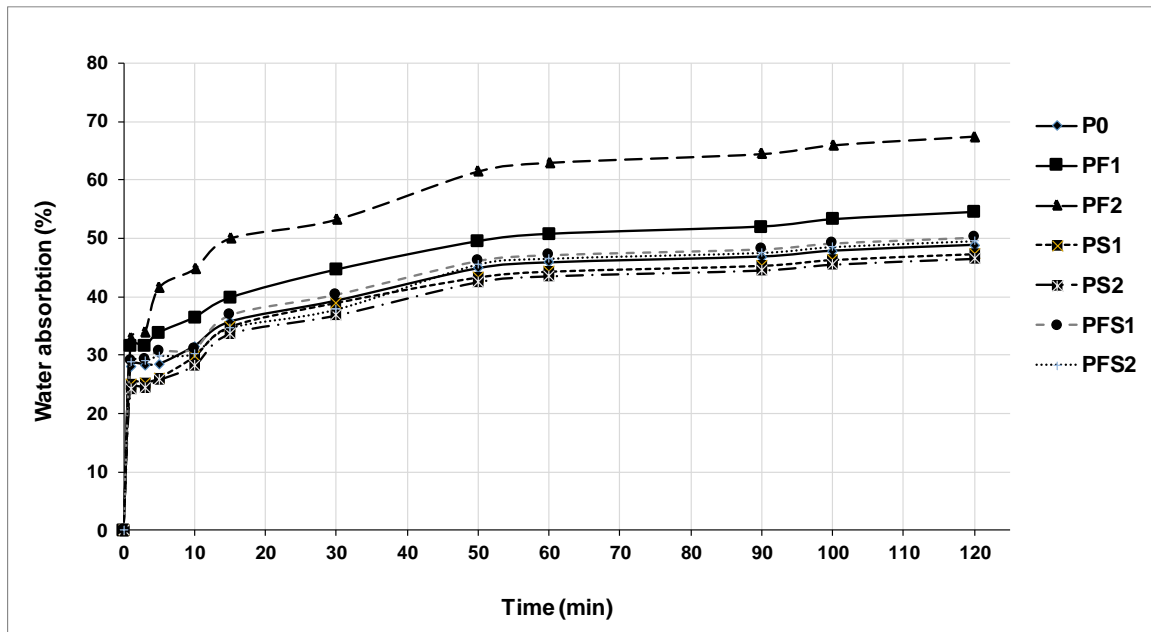


Fig. 1. Moisture absorption curves obtained for films of nanocomposite after 2 hours

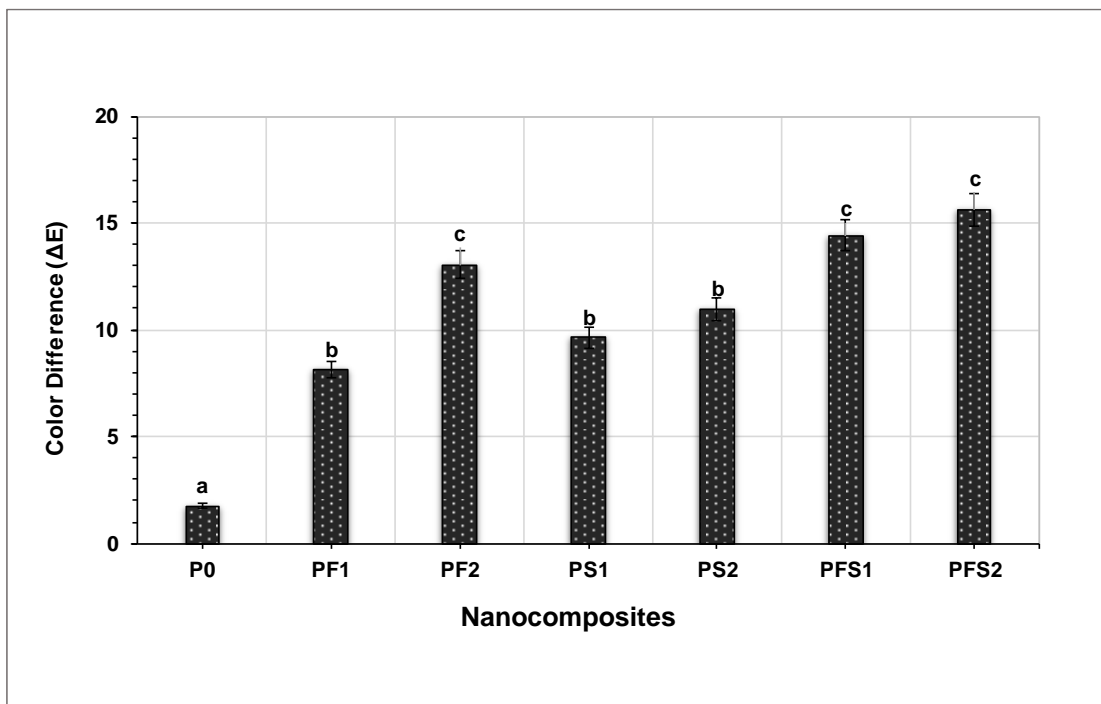
Figure 1 also shows the water absorption test results. In this figure the percentage change is relative to the control sample “P0”, which reflects the effect of adding each amount of nanoparticle on the water absorption characteristic. It was observed that adding 10% and 20% of nano-SiO₂ resulted in better resistance to water absorption than adding 5% and 10% NFC. Results showed that NFC at 20% reduced water absorption more than adding 20% nano-SiO₂. So, adding nano-SiO₂ resulted in better physical performance of the designated nanocomposites. Understandably, NFC is a hydrophilic material, since it originates from the natural fiber, and its hydrophilic nature has been reported by several research studies (Dehnad *et al.* 2014).

The moisture diffusion coefficient is the most important parameter in expressing how water and moisture are absorbed in composites (Pereda *et al.* 2014). Nanometer fillers helped to reduce the absorption by increasing the diffusion path and reducing the pores through the film to improve performance. The results show that the addition of nano-SiO₂ reduced the water absorption. The reason for this reduction is related to the creation of a more cohesive structure and less free spaces due to the addition of nano-SiO₂ as well as less hydrophilicity of nano-SiO₂ compared to NFC and matrix, which reduces the water permeability to films.

Transparency of Composite Films

The addition of nanoparticles caused a change in the optical parameters and color indicators of nanocomposite films. Transparency is a feature of composite films because it directly affects the appearance of the product (Thakur *et al.* 2015). The color differences

of the films ΔE , the whiteness index (WI), and the yellowness index (YI) are reported in Table 2. The intensities of the effects of the independent variables are reported in Fig. 2. The measure values of film samples are presented in Fig. 2. In the figure, the P0 film showed the highest percentage of transparency due to the absence of NFC and silica nanoparticles, followed by nanocomposite films. The lower the calculated ΔE for a sample, the higher the transparency of the film. In this case, the recorded color parameters of the film were closer to the color parameters of the standard screen. The increase of ΔE in nanocomposite films with increasing the concentration of nanoparticles indicates a decrease in the transparency of the films, which is consistent with the results of the light passing test and transparency. According to several studies related to the effect of different nanoparticles on the color indices of nanocomposite films, there are mixed results, which can be due to the different properties and characteristics of nanoparticles.



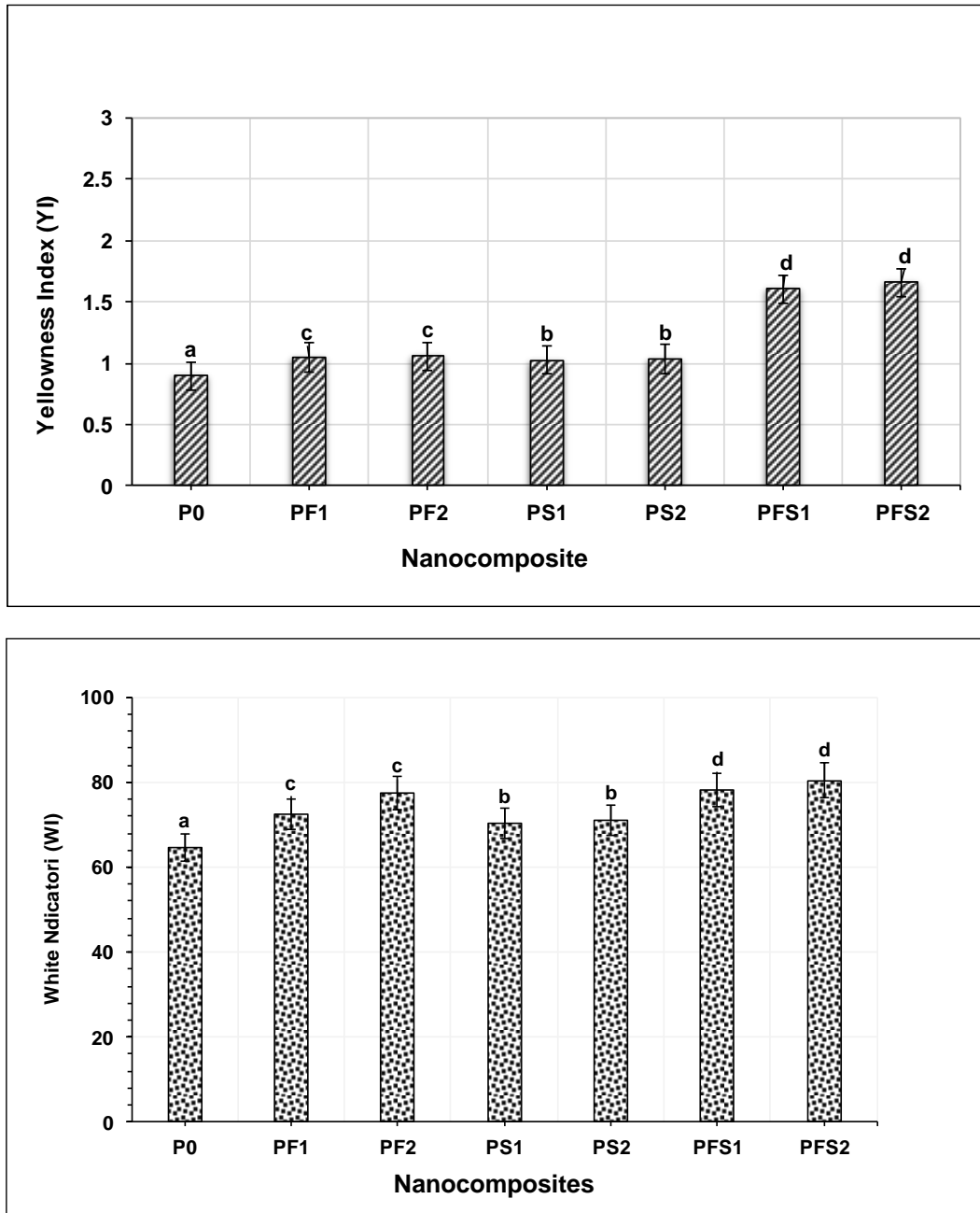


Fig. 2. The effect of nanoparticles on the optical properties index of nanocomposites

Table 2. Summary of Color Parameters of Nanocomposite Films of Adding Nanoparticles

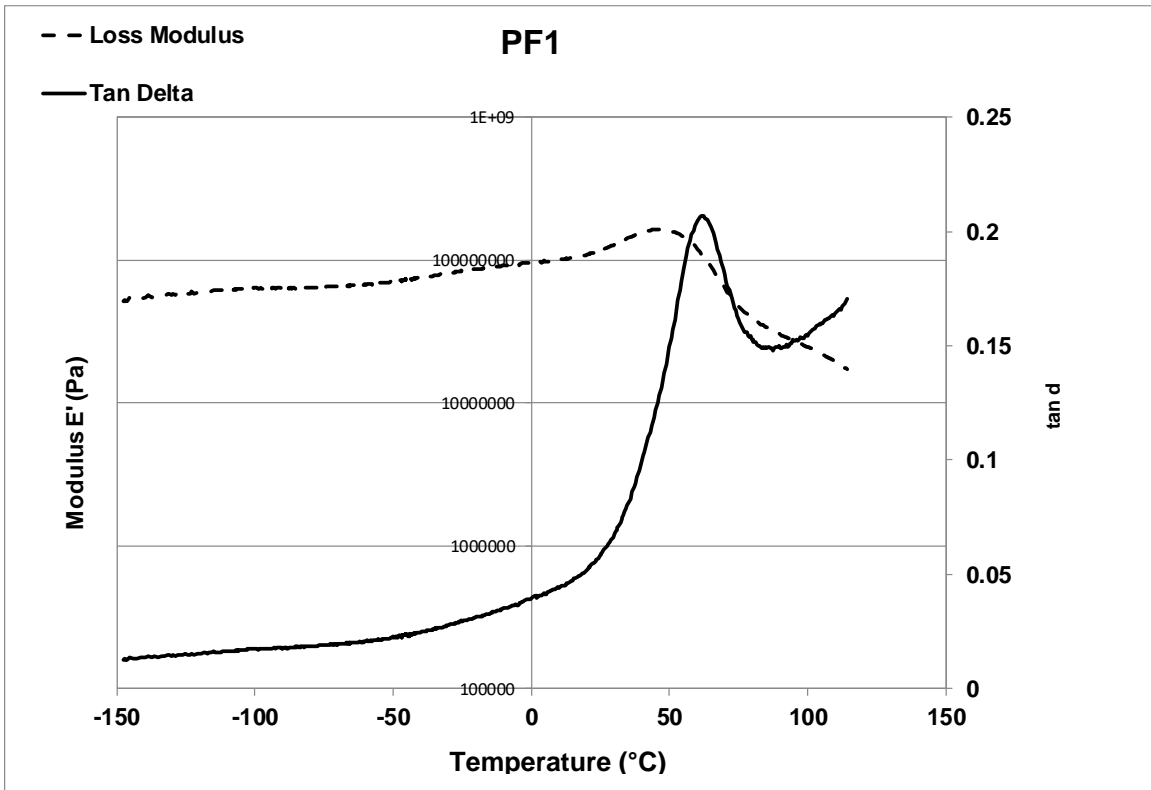
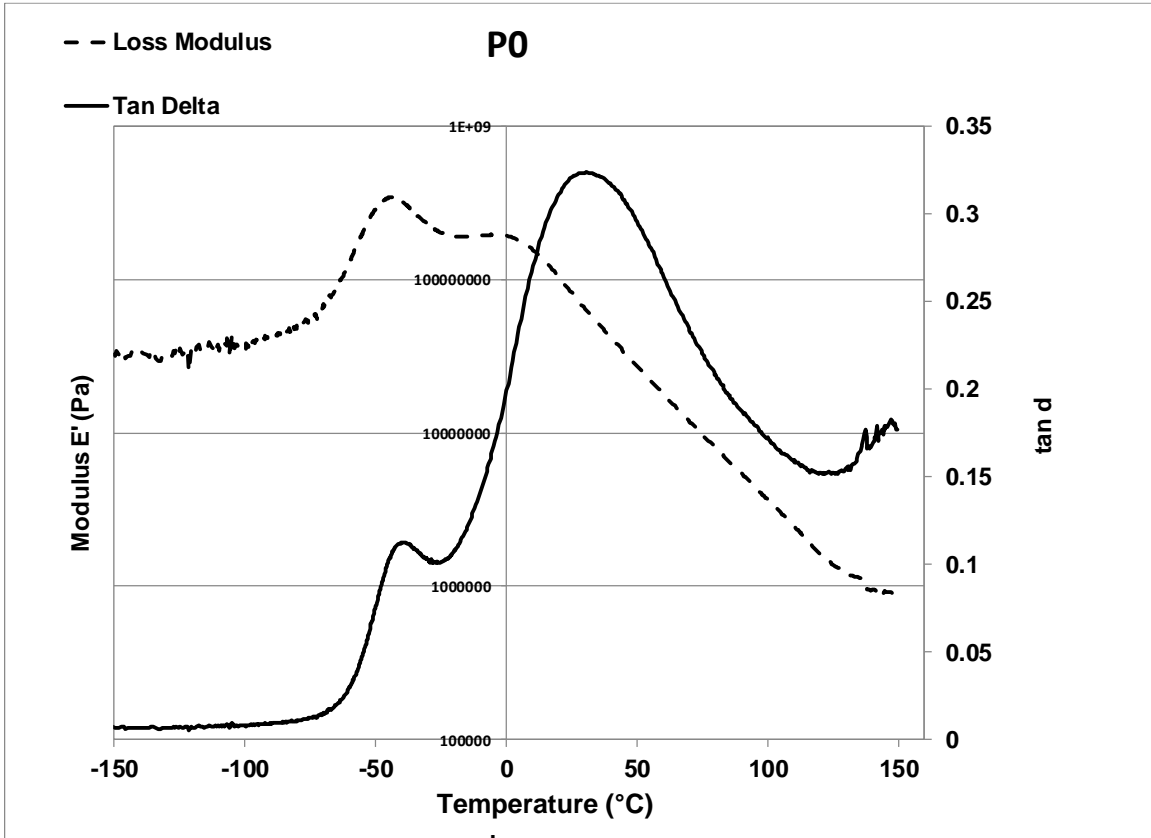
| Nanocomposite Type | Color Difference (ΔE) | White Index (WI) | Yellowness Index (YI) |
|--------------------|---------------------------------|------------------|-----------------------|
| P0 | 1.759 | 64.564 | 0.495 |
| PF1 | 8.145 | 72.483 | 1.048 |
| PF2 | 13.031 | 77.523 | 1.059 |
| PS1 | 9.637 | 70.243 | 1.028 |
| PS2 | 10.982 | 71.224 | 1.035 |
| PFS1 | 14.407 | 78.244 | 1.605 |
| PFS2 | 15.618 | 80.405 | 1.657 |

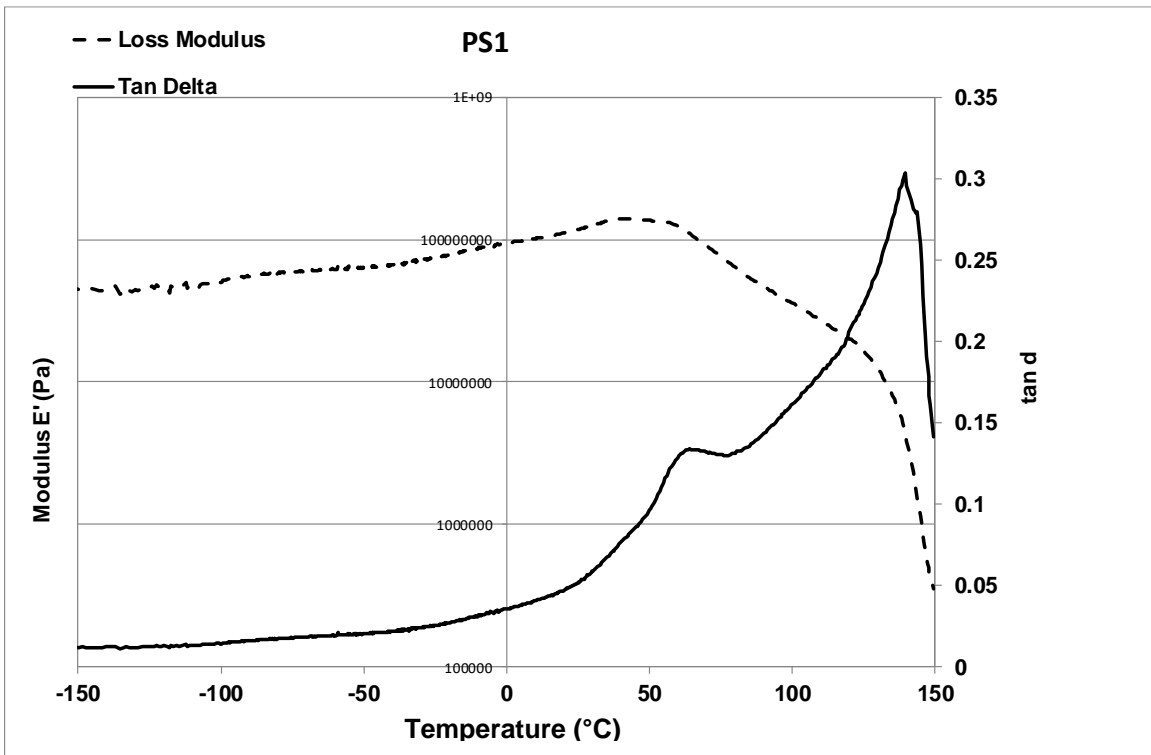
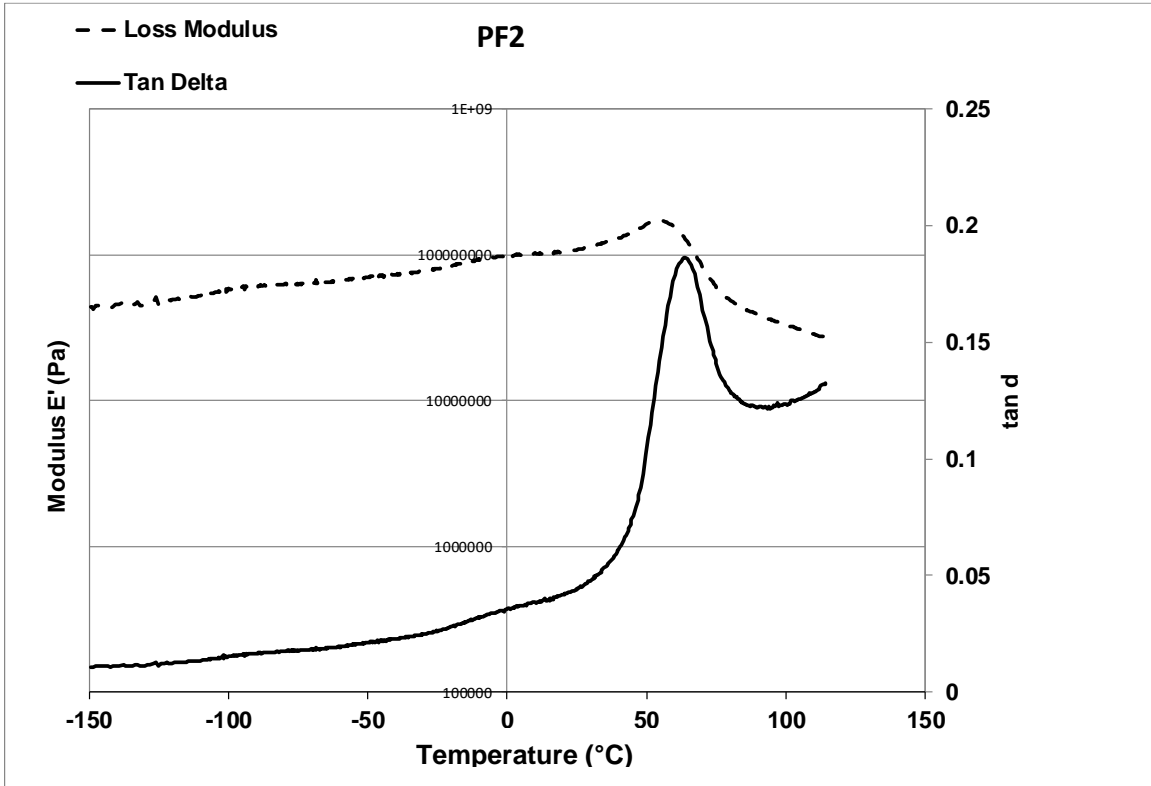
Other descriptive factors include whiteness, yellowness, and chroma index. The yellowness index had a similar change in ΔE due to the addition of nanoparticles to the matrix. There was a significant difference in the whiteness index of the films with the addition of nanoparticles compared to the control sample. In other words, the rate of decrease and increase had a certain trend with increasing the concentration of nanoparticles. In general, based on the results, the increase in the YI value indicated an increase in yellow color in nanocomposites containing high concentrations of nanoparticles. The cause of increased turbidity can be attributed to the addition of nanoparticles and the accumulation of nanoparticles in the polymer substrate. Although the size of nanoparticles is the nanometer range, the agglomeration of nanoparticles in the nanocomposites is inevitable with large loading. This agglomeration can explain why the nanocomposite films displayed a low light transparency with high loading of nanoparticles.

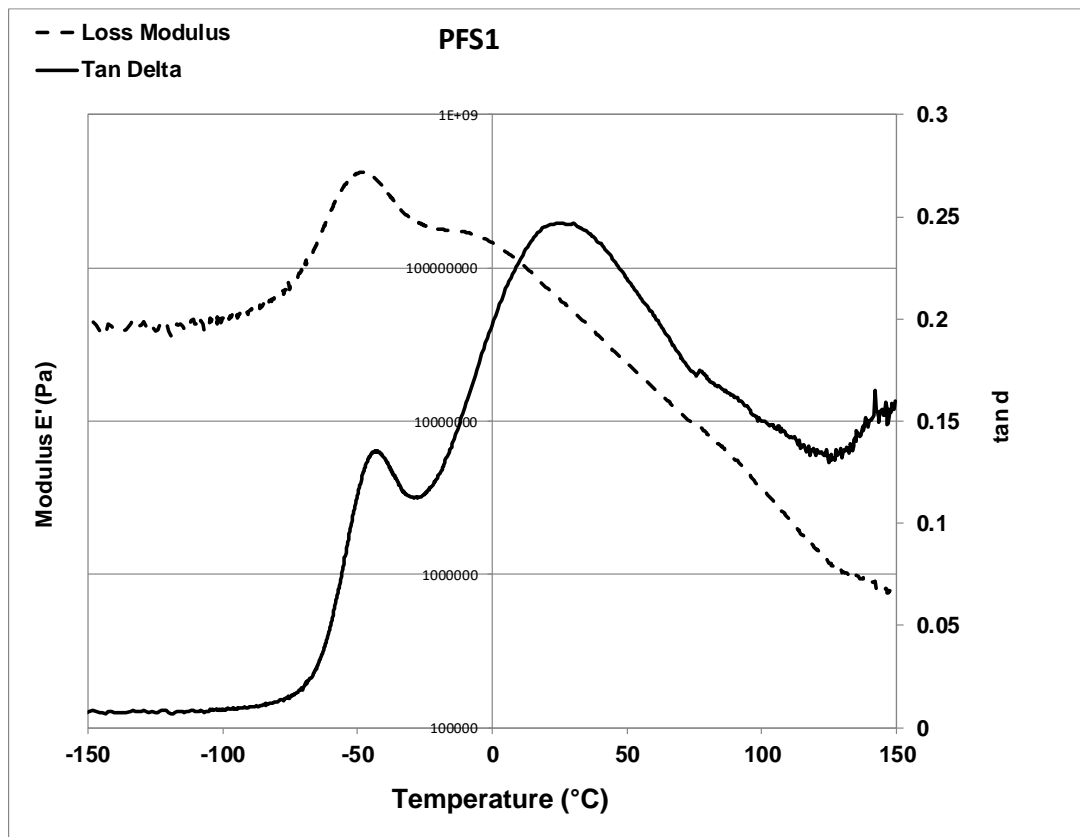
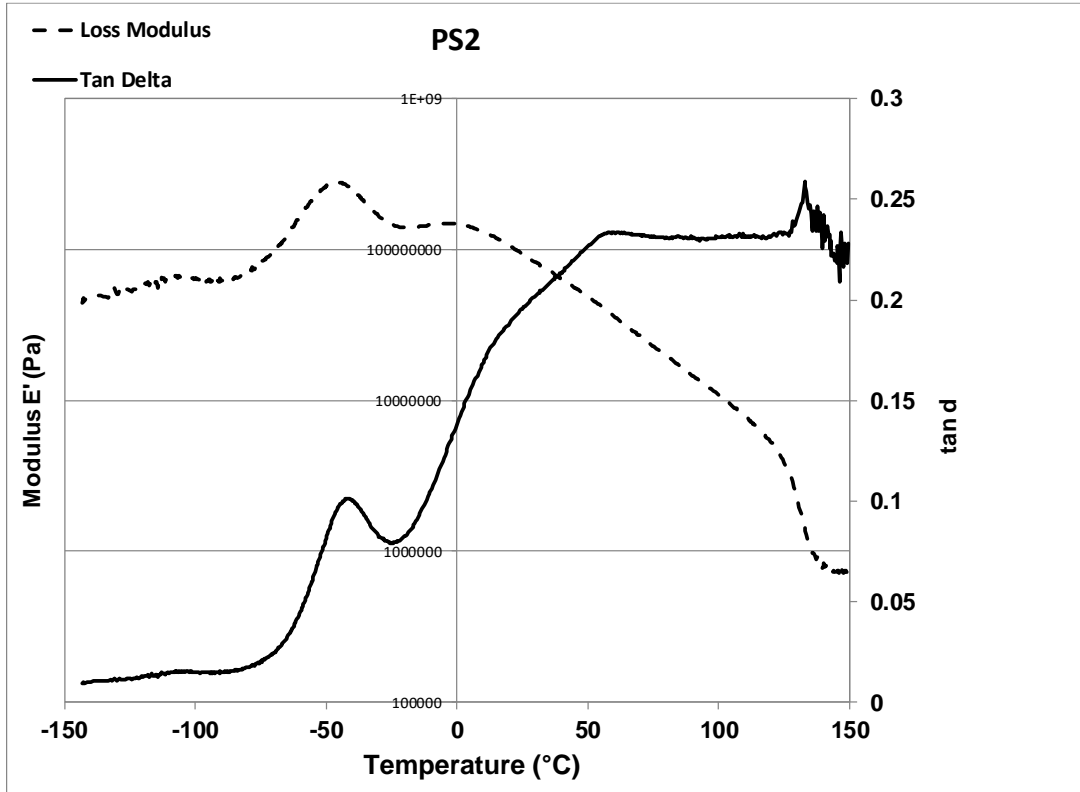
Dynamic Mechanical Thermal Analysis

There are several methods for examining the association between nanoparticles and a polymer matrix. Dynamic mechanical thermal analysis is an important technique for measuring the mechanical and thermal properties of materials such as nanocomposites. Composite materials exhibit the desired properties when the particles are homogeneously distributed within the matrix and distributed without the formation of larger bulk structures. The loss modulus represents the viscous properties, and the storage modulus represents the elastic properties of a material. There are several ways to detect the glass transition temperature. One of these methods uses the maximum loss modulus for rheological tests, as shown in Fig. 3.

DTMA (Triton Technology Model Tritec DMTA 2000, UK) was used to evaluate the dissipation coefficient ($\tan\delta$) and glass transition temperature (T_g). The experiments were performed at temperatures between $-150\text{ }^\circ\text{C}$ and $150\text{ }^\circ\text{C}$, a heating rate of $4\text{ }^\circ\text{C}/\text{min}$, and a load frequency of 1 Hz . The effect of adding silica nanoparticles to composite films on the $\tan\delta$ curve as an indicator for DMTA behavior and glass transition temperature (T_g) extraction is shown in Fig. 3. The shapes of $\tan\delta$ curves for composite types are presented in Fig. 3. Two temperature ranges could also be observed in all $\tan\delta$ curves, which represented low and high glass transition temperatures $T_{g\alpha}$ and $T_{g\beta}$, respectively. The T_g values obtained for samples with different amounts of nanoparticles are presented in Table 3. The lowest amount of ($T_{g\alpha}$) corresponded to the sample without nanoparticles, and the highest amount of ($T_{g\alpha}$) corresponded to the sample containing 10% nano-SiO₂. The highest T_g , $62\text{ }^\circ\text{C}$, of NFC composites was obtained at 20% for the mechanical interlocked structure but dropped with the further increase of NFC and nano-SiO₂ content due to their self-aggregation. The highest T_g was achieved when nano cellulose fibers content was 20 wt%, $62\text{ }^\circ\text{C}$, which was $45\text{ }^\circ\text{C}$ higher than that of neat PVOH and $32\text{ }^\circ\text{C}$ higher than that of PVOH/SiO₂. These findings confirm the important role of NFC in the system. As discussed above, strong hydrogen bonding formed among PVOH, NFC, and SiO₂, slowing down the dynamics of PVOH chains in the vicinity of fillers.







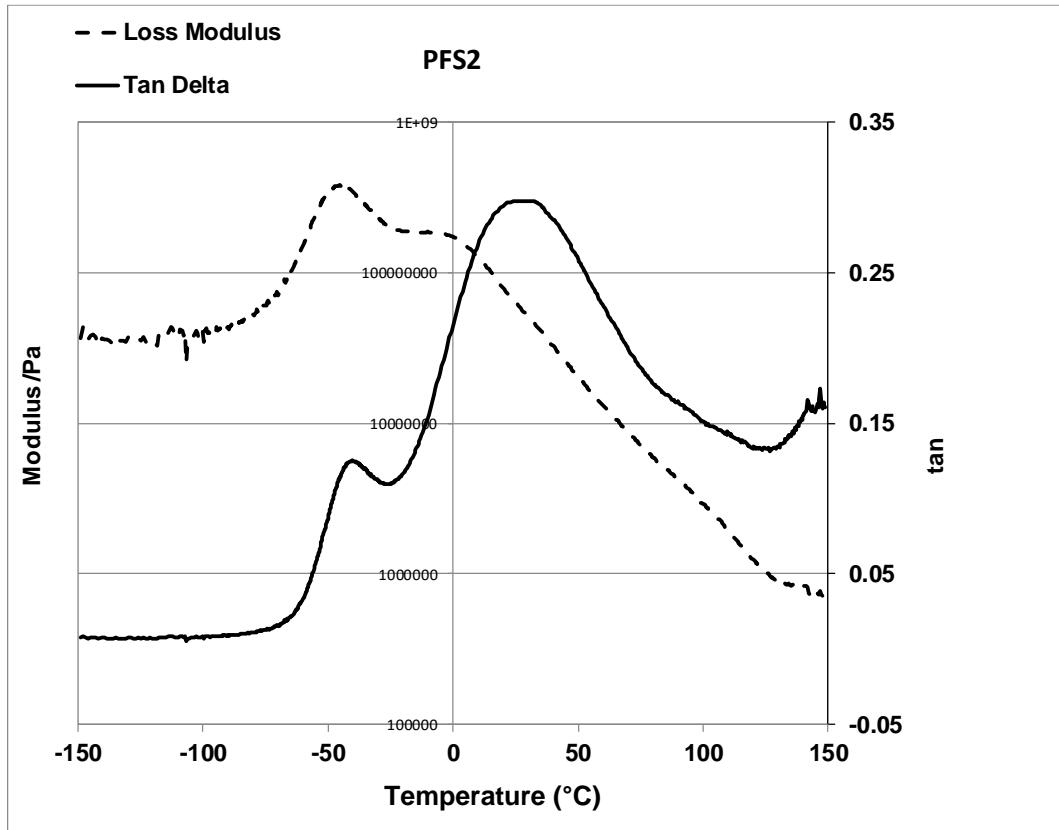


Fig. 3. The $\tan\delta$ curves and loss modulus for nanocomposites with various amounts of nanoparticles

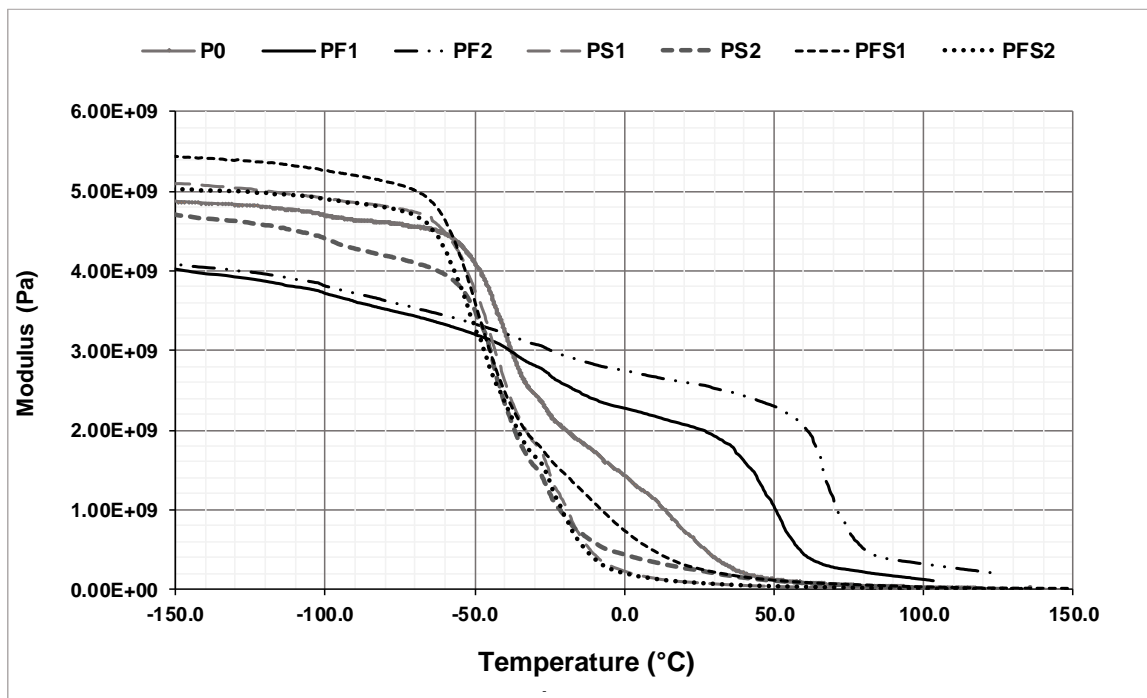


Fig. 4. Storage modulus of nanocomposites

In Fig. 4 the storage modulus of the composites is demonstrated. The modulus of pure PVOH increased with the addition of nanoparticles. This can be ascribed to the enhancement of the stiffness of the matrix. It is also seen from Fig. 4 that nanoparticles influenced the modulus value. The highest values were observed for 5 wt% NFC and 5 wt% SiO₂. In the case of adding nano SiO₂, there were changes in the loading levels of 5 and 10 wt%, and the loading increased the modulus of the PFS₁ composite.

The maximum value of modulus was observed for 5 wt% nano SiO₂ and NFC addition amongst all composites. This was followed by 10 wt% nano-SiO₂-containing PFS₂ composites. Generally, all nanoparticles partially increase the modulus of nanocomposites. As is known, in the case where the interfacial interaction is strong, the mechanical properties are likely to be increased. Moreover, if the nanofibers act as a bridge between the nano-SiO₂ and the matrix, then there will be an increase in the volume fraction of the interface and a decrease in chain mobility of the interface zone of the composite.

Table 3. Glass Transition Temperatures of Designated WPCs

| Sample Type/Nanoparticle Content | $T_{g\alpha}$ (°C) Low Glass Transition Temp. | $T_{g\beta}$ (°C) High Glass Transition Temp. |
|----------------------------------|--|--|
| P ₀ | -108 | 27 |
| PF ₁ | -104 | 61 |
| PF ₂ | -100 | 62 |
| PS ₁ | -37 | 30 |
| PS ₂ | -41 | 56 |
| PFS ₁ | -42 | 32 |
| PFS ₂ | -43 | 58 |

Wettability of Composite Films

Understanding the surface chemistry of nanocomposite film has become critical as the composite in moisture environment have an attractive or repulsive response to water. The surface chemistry determines the wettability of the nanocomposite, where the chemistry behind this process affects the surface tension. The composite film exhibits surface hydrophobicity, which was evaluated by means of contact angle determination. There is an imbalance in molecular forces when moisture droplets are present on the nanocomposite, in this affects the degree of wetting. The property of wettability and water-repellent enhancement of the nanocomposite samples can be determined by measuring the contact angle of liquid on the surface of the composites. Contact angle is one of the basic features for composite films, which reflects the wettability properties and determines water resistance. Regarding the contact angle, two modes can be considered. Firstly, if the surface adhesion force is more than the cohesion force, then the liquid spreads on the surface and makes it wet. In this case, the contact angle is less than 90°. Moreover, if the adhesion force is less than the cohesion force of the liquid, then the liquid remains on the surface as separate droplets and does not cause wetness. In this case, the contact angle is more than 90°. Figure 5 shows the images of contact angle on nanocomposites with pure PVOH and NFC and nano-SiO₂ for 0%, 5%, and 10% of the samples.

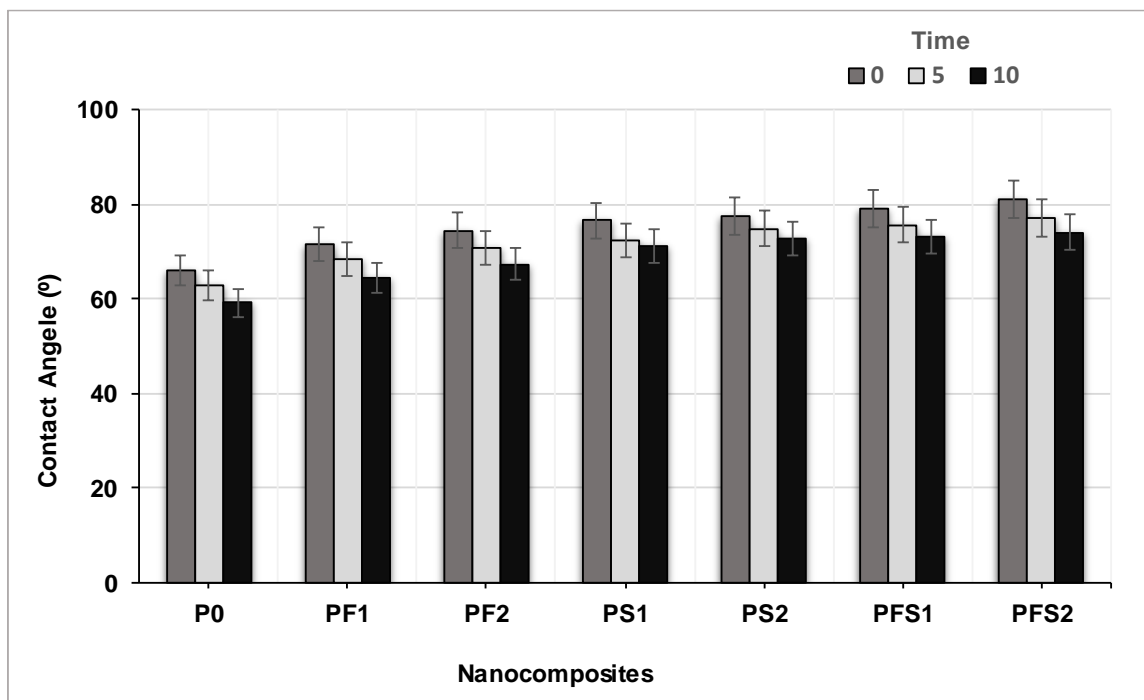
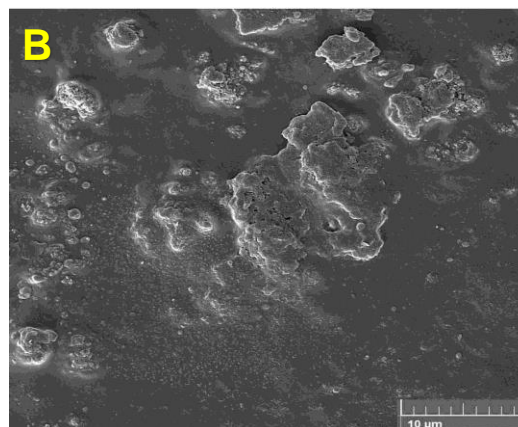
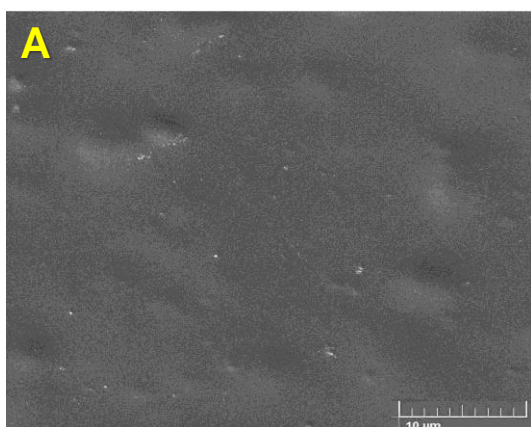


Fig. 5. Contact angle of neat PVOH and various types of nanocomposite films

The contact angles of composite films increased from 66° to 71° , 74° , 76° , and 77° , 79° , 81° , with an increase in the nanoparticle content from 0 to 5, and 10 wt%, respectively. The contact angle of the pure film without nanoparticles was about 73° , which indicated the inherent hydrophilicity of this polymer. Addition of 5% nanoparticles, the contact angle increased, which indicated that the change in the contact angle of the films occurred, and its increase was negligible. Increase in the NFC and nano-SiO₂ content from 0 to 5, 10 wt%, respectively. These results indicate that the hydrophobicity of nanocomposite film was higher than the PVOH film. This phenomenon can be attributed to decreased surface energy, and higher surface roughness as a result of nanoparticle addition could contribute to increased hydrophobicity of nanocomposites (Lee *et al.* 2009). The extensive hydrogen bonding between polymer matrix and NFC may disfavor the hydrogen bonding sites for water molecules (Kisonen *et al.* 2015).



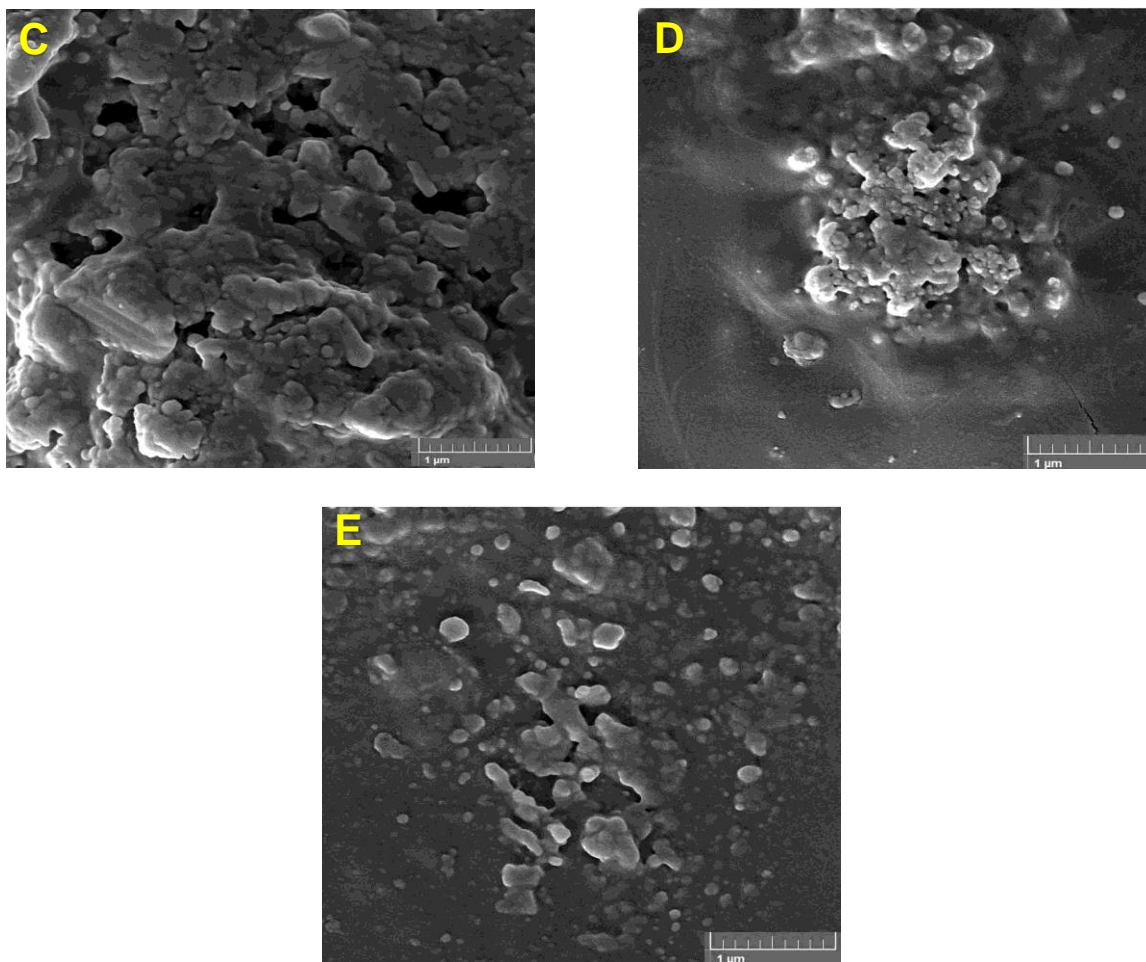


Fig. 6. SEM micrographs of fracture surface of composite films: A) PVOH, B) PS1, C) PFS1, D) PFS2, and E) PS2

Morphology of Composite Films

Microphotographs of nanoparticles-reinforced PVOH composite are shown in Fig. 6C. Voids signify the amount of NFC and nano-SiO₂ for PSF1 composite. The images show that fracture surfaces were rougher for the nanocomposites, compared to the neat PVOH films. The white dots, having different sizes, on the nanocomposites, can be considered as nano-SiO₂. The amount of these smaller white dots was found to be increased with increasing nano SiO₂ content, indicating that these became dispersed in the PVOH matrix. In Fig. 6D, the number of voids decreases with increasing nano-SiO₂ content. Furthermore, the processing route used, which involved sonication followed by solution-casting, can be considered as an efficient method to distribute nanoparticle reinforcements in PVOH matrix.

CONCLUSIONS

1. Due to increasing the amount of nano-silicon dioxide in the matrix, the water absorption of nanocomposites decreased and led to better dimensional stability.
2. The addition of nanofibrillated cellulose (NFC) and nano-silicon dioxide led to thermal resistance and led to higher glass transition temperatures (T_{gp}).
3. Scanning electron micrograph (SEM) images showed that nanoparticles were uniformly distributed in the PVOH matrix. The sonication was found to be effective, leading to stronger and more efficient nanoparticles-PVOH bonding.
4. Transparent films, in the case of pure PVOH, became increasingly opaque with increasing nanoparticles contents, although the composites also retained moderate transparency.
5. Adding nanoparticles to the matrix caused an increase of contact angle, because NFC and nano-silicon dioxide provide a more surface roughness path to water passing through the film.

ACKNOWLEDGEMENTS

The authors are grateful for the support received of the Islamic Azad University, Science and Research Branch of Tehran, Iran. Special thanks of Expert in charge of laboratory Tarbiat Modares University (Manzar Haghdoost), for providing the facilities for preparing the nanocomposites.

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Article submitted: October 1, 2021; Peer review completed: November 20, 2021; Revised version received and accepted: December 8, 2021; Published: December 16, 2021.
DOI: 10.15376/biores.17.1.1031-1046