NANOFIBRILLATED CELLULOSE (NFC) REINFORCED POLYVINYL ALCOHOL (PVOH): PROPERTIES AND SOLUBILITY OF CARBONDIOXIDE

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Abstract

Polyvinyl alcohol (PVOH) was mixed with an nanofibrillated cellulose (NFC) fiber suspension in water followed by casting. The transmission electron scanning (TEM) images revealed that the NFC fibers dispersed well in PVOH. It was found that the presence of NFC could significantly increase the tensile modulus of the nanocomposites nearly threefold. The differential scanning calorimetry (DSC) analysis showed that the NFC could serve as a nucleating agent, promoting the early onset of crystallization. However, at a higher NFC content, it also led to greater thermal degradation of the PVOH matrix. The nanocomposites were found to be sensitive to moisture content and dynamic mechanical analysis (DMA) tests showed that at room temperature, the storage modulus increased with decreasing moisture content. The solubility of carbon dioxide (CO_2) in the nanocomposites depended on their moisture content and decreased with the addition of NFC. Moreover, the desorption diffusivity became higher as the amount of NFC increased.

Introduction

In recent years, environmental concerns have led to an escalated interest in natural fibers and biodegradable polymers. At the same time, new technologies originating from the field of nanosciences have engaged and opened opportunities in many areas, including forest product technology[1]. For instance, wood structure cell walls are composed of several layers. Each of these layers is composed of cellulose MFs, aligned in an ordered, parallel arrangement, which differs from layer to layer. Cellulose MFs are, however, tightly hooked to one another by multiple hydrogen bonds. Mechanical homogenization, or shearing, has been used to break the bond. When dispersed in water, the suspension is called nanofibrillated cellulose (NFC) [2-5].

NFC is gaining attention as a reinforcing filler in thermoplastic matrices due to its numerous advantages, which include low density, renewable in nature, high specific properties, biodegradability, gas barrier properties, and unlimited availability [6-10]. Despite these attractive properties, the processing temperature of composites is restricted to about 200°C because of NFC degradation, thus restricting the type of matrix that can be used in association with natural fiber [11].

In this study, polyvinyl alcohol (PVOH), a biodegradable, water soluble polymer, was chosen to produce the cellulose-reinforced composites. Moreover, both PVOH and NFC are also known for their good gas barrier properties [8-10, 12-14]. Low polarity gas molecules, such as oxygen and carbon dioxide, exhibit only weak interactions with the highly polar hydroxyl groups in PVOH, resulting in the good gas barrier properties of PVOH [15]. When there are no pores to allow for gas flow through a material, the gas permeability will depend on the dissolution of oxygen and its rate of diffusion in the particular material [8]. However, no study has investigated the sorption of CO_2 in PVOH and PVOH/NFC nanocomposites. It is therefore of interest in this study to measure the solubility of CO_2 in PVOH and PVOH/NFC nanocomposites.

Experiments

Materials

NFC was received from Forest Products Laboratory, Madison, WI. It was prepared according to a procedure described by Saito and Isogai [16]. Fully bleached Kraft eucalyptus fibers were oxidized with sodium hypochlorite using tetramethylpiperidine-1-oxy radical (TEMPO) sodium bromide as a catalyst. The TEMPO-mediated oxidation was carried out at a pH of 10 at 25°C for 3 hours. The fibers were then thoroughly washed and refined in a disk refiner with a gap of approximately 200 µm. The coarse fibers were separated by centrifuging at 12,000 G force, and the nanofiber dispersion was concentrated to 1% using ultrafiltration. A final clarification step was performed in which the nanofiber dispersion was passed once through an M-110EH-30 microfluidizer (Microfluidics, Newton, MA) with 200 µm and 87 µm chambers in series.

Commercially available partially hydrolyzed (87 to 89%) polyvinyl alcohol (PVOH), Celvol 502®, was purchased from Celanese Chemicals, Ltd. It had a Mw in the range of 13,000 to 23,000 and a degree of polymerization of 150 to 300.

Processing

NFC slurry was diluted with deionized (DI) water When the NFC was thoroughly dispersed by magnetic stirring for 30 minutes, an adequate amount of PVOH was added, and stirring was kept for 2 hours on a hotplate at a set temperature at 60ºC to dissolve PVOH and let the

polymer penetrate into the cellulose network. At 0, 2.5, 5, and 10 wt%, NFC and PVOH were prepared. Then, the mixture was casted in a Petri-dish with a diameter of 90 mm and dried at room temperature (about 25°C) and atmospheric conditions (relative humidity of around 50 ± 5%) for seven days. Sample thicknesses were approximately 0.8 mm. Samples were further kept at 90% humidity and 80°C to equilibrate the moisture content in all samples prior to further treatment or test.

A transmission electron microscope (TEM, LEO 912) was used to characterize the dispersion of NFC. Nanocomposite specimens (PVOH +10%NFC) were cut into 50 to 70 nm slices via an ultra-microtome at room temperature. The TEM was operated at 120 kV at room temperature.

Tensile Testing

The specimens from the 90% humidity room were punched out using an ASTM D638 Type V cutting die. Prior to testing, samples were kept in the testing room (50% humidity at 25ºC) for 4 days. The static tensile modulus, strength, and strain-at-break were measured on an Instron 5865. Tensile testing was performed on all specimens using an initial load of 2 N and a constant crosshead speed of 10 mm/min.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed on a DSC Q20 (TA Instruments). The specimens used for DSC characterization were taken from the 90% humidity room to a 30% humidity room for 4 days prior to DSC testing to reduce the moisture content in the samples. Specimens of 6 to 8 mg were placed in aluminum sample pans and heated from 30°C to 205°C at a 10°C/min heating rate and held at 205°C for 2 min to eliminate the thermal history. Specimens were then cooled at 10°C/min to 30°C. The specimens were then reheated to 205°C and cooled down to room temperature using the same heating, holding time, and cooling rates. The crystallization temperature (T_c) was determined from the DSC cooling curves.

Thermogravimetric Analysis (TGA)

Samples used for thermogravimetric analysis (TGA) were dried at 90°C for 2 days. TGA was performed by using a TGA Q50 (TA Instruments) from 25º to 600°C at a heating rate of 10°C/min. Approximately 10 mg of composites were used. The loss of weight was recorded and normalized against the initial weight.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) measurements were performed on a DMA Q800 (TA Instruments) in single cantilever mode. The specimens from the 90% humidity room were prepared to dimensions of approximately 35.2 by 12.7 by 0.8 mm and then kept in the testing room (50% humidity at 25ºC) for 4 days before the test. During the DMA test, the specimens were heated at a rate of 3°C/min from –20ºC to 150ºC with a frequency of 1 Hz and amplitude of 50 µm. In the study on the effect of moisture content on the dynamic mechanical properties, additional specimens were dried in an oven at 90ºC for 2 days prior to DMA testing.

Sorption Measurement

The main purpose of the sorption experiments was to establish the amount of CO_2 absorbed in the PVOH and PVOH/NFC nanocomposites. The original weights of these samples were measured using a digital balance readable to 0.0001 g and the sorption of CO_2 into the specimens was done in a high pressure vessel at 800 psi at room temperature for 1 day. At the end of the sorption, the vessel was depressurized and the CO_2-absorbed samples were removed from the pressure vessel and weighed on the balance for recording weight changes and weight loss as a function of time during desorption at atmospheric pressure. The process of taking the samples in the pressure to the balance took around 40s. Samples were kept in an oil bath on the scale to reduce the weight gain or loss in the sample due to moisture. The diffusivity of gas (D) in the sample was given by the following equation [17, 18],

$$D = \frac{\pi}{16}\left[\frac{d\left(\frac{M_t}{M_\infty}\right)}{d\left(\frac{\sqrt{t}}{l}\right)}\right]^2 \qquad (1)$$

where M_t is the amount of gas lost at time t, M_∞ is the mass uptake at infinite time, and l is the thickness of the sample.

Results and Discussions

Dispersion of NFC in PVOH

Figures 1 show the TEM images of the cut sample via ultra-microtome.

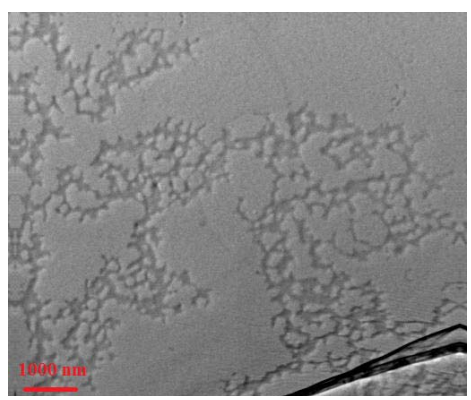

Figure 1. TEM images for nanocomposites. Sample was obtained by cutting via ultra-microtome.

The TEM images illustrated that NFC was an interconnected web having a diameter in the range of 10 to 50 nm. When dispersed in water, NFC formed a very stable suspension due to the strong hydrophilic characteristics of cellulose. Based on the TEM images, it was concluded that NFC dispersed well in a PVOH water solution. Further evidence for the uniformity of the dispersion was the transparency of the resulting film.

Tensile Properties

The influence of different concentrations on well dispersed NFC implied that tensile properties of the composites could be affected. Tensile tests (according to ASTM-D-638-02) were performed on punched specimens. The representative stress–strain curves were featured in Figure 2.

As seen from Figure 2, the addition of NFC yielded stronger and stiffer composites but toughness (measured as work of fracture) was reduced in comparison to neat PVOH samples. The strain-at-break of PVOH, PVOH + 2.5% NFC, PVOH + 5% NFC, and PVOH + 10% NFC were found to be 4.36, 3.20, 2.59, and 0.61, respectively. The less than desired strain at break of PVOH nanocomposites was probably due to PVOH itself reaching its maximum tensile strength. Likewise, neat PVOH had the lowest value of ultimate tensile strength and tensile modulus which were 16.12 and 25.48 MPa, respectively. As the amount of NFC increases, the ultimate tensile strength and the tensile modulus increased.

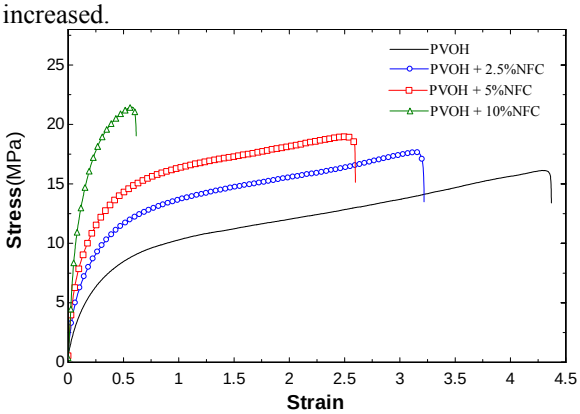

Figure 2. Tensile stress versus strain curve for the NFC and PVOH composites.

Thermal Properties

PVOH is a semicrystalline polymer in which high physical inter-chain and intra-chain interactions exist, due to hydrogen bonding between hydroxyl groups. The introduction of nanosized NFC with hydroxyl groups alters the intra-molecular and inter-molecular interactions of the PVOH chains. This may affect both the crystallization behavior and the physical structure of PVOH, resulting in the variations in properties of composite samples [19].

Because the PVOH decomposition temperature is below its melting temperature, the first and second cooling cycles were compared in this experiment [12, 13]. The first and second cooling cycles are plotted in Figure 3.

An exothermic peak around 160° to 170 ºC was observed in all specimens corresponding to the crystallization of PVOH (cf. Figure 3). The additional thermal treatment between the first and second scans caused a shift of the crystallization temperature to a lower temperature, thereby lowering the heat released with crystallization. Both of these effects were attributed to sample degradation [20]. The magnitude of the shift increased with increasing NFC concentration, thus indicating that NFC might promote degradation of the polymer. These degradation results were further confirmed by the TGA results. Moreover, it was clear that with the addition of 2.5% NFC, the crystallization peak of PVOH shifted to a higher temperature and the crystallization regime was prolonged as compared to neat PVOH. The observed effects can be attributed to the nucleating effect of NFC in the PVOH crystallization process. The addition of NFC (i.e., 5% and 10%) to the composites reduced the increase of the crystallization peak temperature, thus indicating that NFC might influence the degradation of PVOH. Similar results of the effect of nanosized materials on the crystallization and degradation of PVOH have also been suggested [19, 20]. In addition, the shoulders around 50°C to 80ºC in the DSC thermograms in Figure 3 revealed the glass transition temperature of the PVOH nanocomposites.

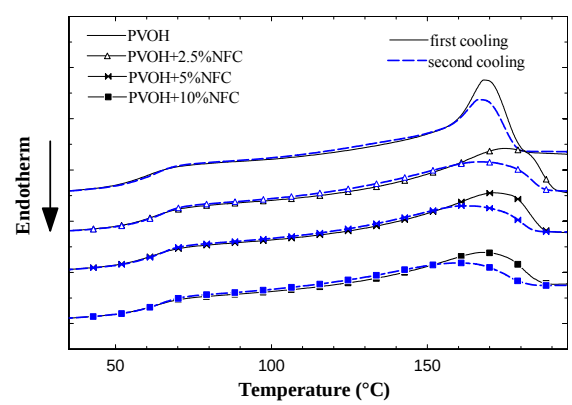

Figure 3. Comparison of the crystallization exotherms during the first (solid line) and second (dashed line) cooling scans of PVOH, PVOH+2.5%NFC, PVOH+5%NFC, and PVOH+10%NFC.

Thermal Stability

The thermal stability of the neat PVOH and PVOH/NFC composite samples were examined using TGA. TGA results shown in Figure 4 confirm that NFC leads to increased degradation. The onset degradation

temperatures of the composites decreased with the addition of NFC.

For 100% NFC, it was assumed to be that of a dried NFC film prepared by evaporation of water from a NFC suspension and dried at 90ºC for 2 days. As shown in Figure 4, weight loss of 100%NFC occurred slowly until around 200ºC, which might be attributed to both the loss of moisture in the NFC as well as the slow degradation of NFC. The most pronounced degradation happened at approximately 200ºC, which was lower than 205 ºC, the heating scan in DSC. There was an approximate 30% char yield at temperatures above 500ºC.

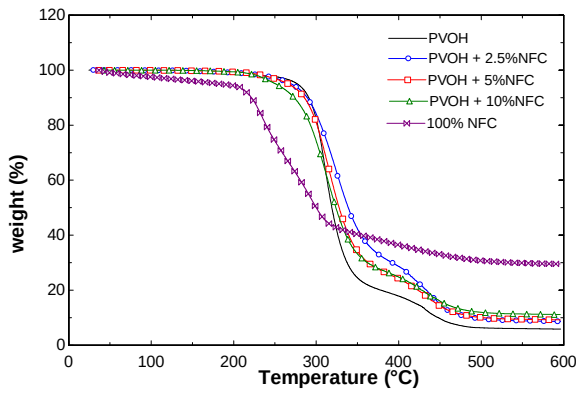

Figure 4. TGA curves for the PVOH/NFC composite samples.

Dynamic Mechanical Properties (DMA)

Since PVOH is a hydrophilic polymer, its properties were strongly affected by the presence of moisture content in the samples [21, 22]. In the study on the effect of moisture content in PVOH and NFC on the mechanical properties, two sets of specimens were prepared. The first set was conditioned in the testing room (50% humidity at 25ºC). Samples were taken from the 90% humidity room to the testing room 4 days before the DMA test. The other set of samples was dried at 90ºC for 2 days prior to the DMA test.

The logarithm of the storage modulus for PVOH nanocomposites prepared at different moisture content levels as a function of temperature are shown in Figure 5. At low temperatures, it was difficult to observe any change in the storage modulus. In the glassy state, the tensile storage modulus *E* slightly decreased with temperature but remained roughly constant. Then, the modulus dropped at a temperature that depended on moisture conditions (around 25 to 40ºC). The modulus dropped later for the samples that had higher moisture content. For samples containing a lot of moisture(Figure 5(a)), the rubbery modulus was found to increase with temperature. This behavior might be because of the concomitant loss of moisture content during the DMA test. On the other hand, for dried samples (Figure 5(b)) at higher temperatures, the modulus dropped consistently. Regardless of the moisture content, the addition of NFC increased the rubbery modulus of the PVOH matrix [22, 23].

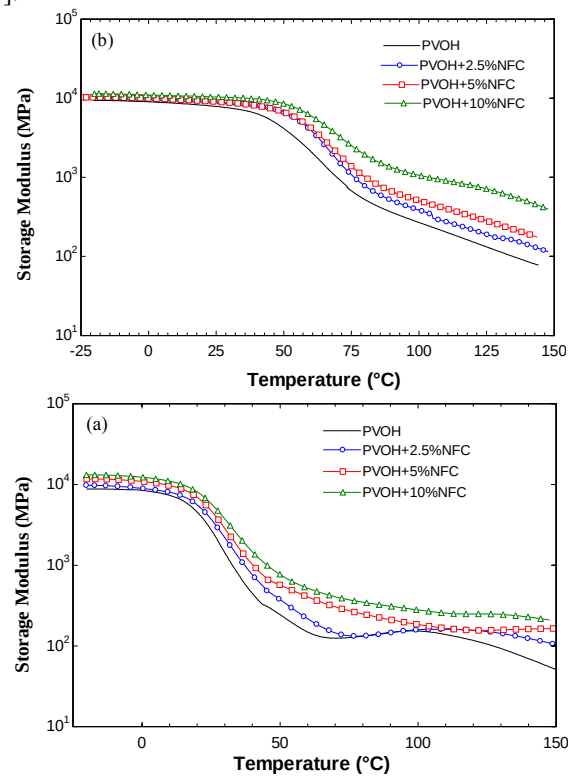

Figure 5. Storage moduli of the PVOH/NFC composite samples. (a) Samples were conditioned at 50% humidity at 25ºC. (b) Samples were dried at 90ºC for 2 days

The differences in mechanical properties can be attributed to the change in the glass transition temperature (T_g) which can be obtained from the peaks of the tan-δ curves in Figure 6. T_g shifted to a lower temperature as the moisture content in the samples increased owing to the well-known plasticizing effect of water molecules on PVOH chains [22]. Moreover, the shift of the peak position was observed upon the addition of NFC, regardless of the moisture content. For samples conditioned at 50% humidity, the peak position for PVOH was at 34.10ºC and increased to 36.05ºC for the composites with 10% NFC. It was also found in Figure 6 that the magnitude of the relaxation process strongly decreased with increasing NFC content. This indicates that fewer polymer chains participated in the transition. The increase in modulus, together with positive shift in the tan-δ peak position, can be attributed to physical interaction between the polymer and reinforcements that restricted the segmental mobility of the polymer chains in the vicinity of the nano-reinforcements [13, 24]. It may also be noted that results from the viscoelastic behavior of the composites agreed with mechanical properties, suggesting that the reinforcing effect of nanofibers in PVOH led to a restriction of molecular chain mobility.

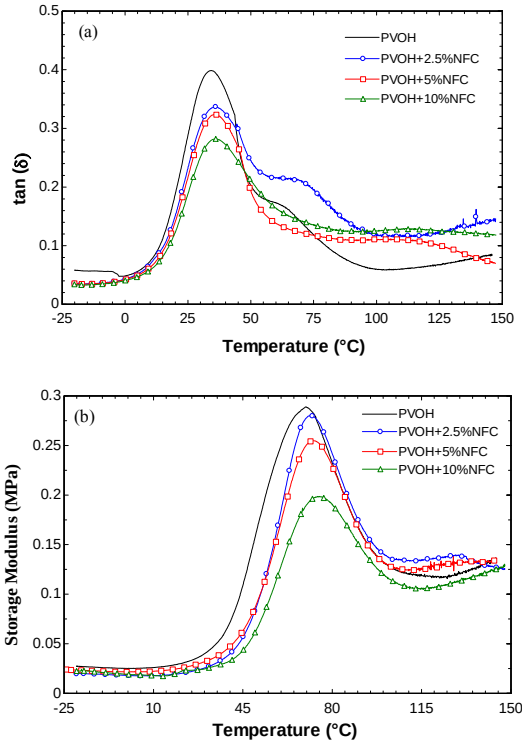

Figure 6.Tan-δ curves of the PVOH/NFC composite samples. (a) Samples were conditioned at 50% humidity. (b) Samples were dried at 90ºC for 2 days.

Sorption Behavior of CO_2 in PVOH

Casted PVOH and PVOH/NFC nanocomposite samples with different moisture contents were originally weighed on a 4-digit scale and then placed in a pressure vessel filled with CO_2 for one day. After depressurization, they were placed on the scale to determine the amount of CO_2 absorbed or the measured solubility and weight loss as a function of time. Samples with low moisture content had low absorbed CO_2 and low weight loss as a function of time. However, samples with high moisture content (i.e., those from the 90% humidity room) had much higher CO_2 absorbed. This means that the solubility of CO_2 in PVOH and PVOH/NFC nanocomposites depended on the moisture content in the samples as the permeability of CO_2 to PVOH increased with higher moisture content as reported in other studies [25, 26]. Therefore, in this experiment, only samples from the controlled 90% humidity room were used.

Figure 7 shows the plot of the CO_2 mass uptake or measured solubility of CO_2 (%) in PVOH and PVOH/NFC nanocomposites with different contents of NFC. The addition of NFC blocked the gas molecules from entering into the matrix. Thus, the solubility of CO_2 in the specimens became lower as NFC content increased [9, 27]. Neat PVOH from the 90% humidity room was found to have 3% CO_2 solubility. With the addition of 10% NFC, the solubility of CO_2 decreased by as much as 33%.

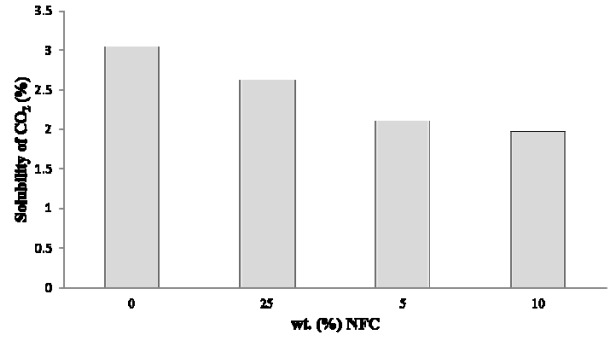

Figure 7. Solubility of CO_2 in PVOH and their nanocomposites with 2.5, 5, and 10 wt% NFC.

The desorption isotherm for CO_2 in neat PVOH and PVOH/NFC nanocomposite samples from the 90% humidity room at atmospheric pressure during the first hour is illustrated in Figure 8(a). During the first period of the desorption process, the mass of CO_2 had a linear relationship with time. Furthermore, the slope became higher as the NFC content increased. Hence, the desorption diffusivity (*D*) became higher as the amount of NFC increased, as can be calculated using Eq. (5). The value of *D* can be calculated from the initial gradient of a curve of M_t/M_∞ plotted versus $t^{1/2}/l$ as shown in Figure 8(b). The *D* values were approximately 3.14×10^{-8}, 5.27×10^{-8}, 2.15×10^{-7} and 6.84×10^{-7} cm^2/s for PVOH, PVOH + 2.5% NFC, PVOH + 5% NFC, and PVOH + 10% NFC, respectively.

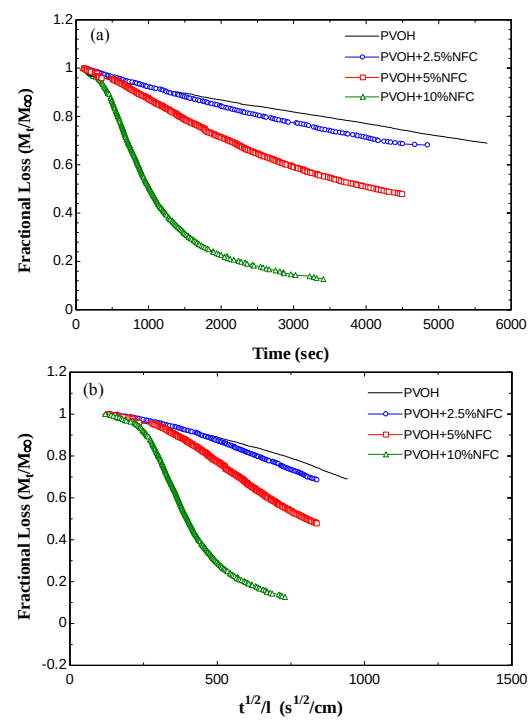

Figure 8. Desorption curves for CO_2 in PVOH and PVOH/NFC nanocomposites during the first hour.

Conclusions

NFC dispersed well in PVOH by blending a suspension of NFC with a solution of PVOH followed by a casting/evaporation technique. NFC had a reinforcing effect on the PVOH, as observed via both DMA and tensile tests. However, toughness decreased as the amount of NFC increased. The addition of NFC to PVOH was shown to nucleate crystallinity and increase the glass transition temperature, but it also caused thermal degradation of the polymer, likely due to the moisture content. The sorption degree of CO_2 in nanocomposites was dependent on the moisture content in the sample as solubility increased with a higher moisture content. The solubility was around 3% in neat PVOH from the 90% humidity room and became lower as the amount of NFC increased. Moreover, the desorption diffusivity became higher as the amount of NFC increased.

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