Chapter 13

# POLYVINYL ALCOHOL BASED BIODEGRADABLE POLYMER NANOCOMPOSITES

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### ABSTRACT

Most commercial polymers and composites used today are prepared using nonbiodegradable constituents. These materials, at the end of their useful life, cannot be easily consumed and simply pile up as waste causing significant damage to the environment. This concern has forced the development of environmentally friendly materials in recent years. Biodegradable materials are generally defined as those polymers and their composites that can decompose in natural environments. Biodegradation of these materials can be achieved by enabling microorganisms in the environment to metabolize the materials to produce an inert humus-like material that is less harmful to the environment and can get easily blended with the natural soil. In our research, a biodegradable polymer polyvinyl alcohol (PVA) was utilized as a matrix resin to fabricate PVA based biodegradable polymer nanocomposites using different nanomaterials. Their properties, relating mechanisms and corresponding applications were deeply investigated. Nanomaterials, including fully degradable bacterial cellulose (BC) and microfibrillated cellulose (MFC), and natural occurred clay halloysite nanotubes (HNTs) were used in biodegradable PVA resin to fabricate biodegradable polymer nanocomposites using solvent intercalation approach. BC-PVA nanocomposites are continuous fiber composites, MFC-PVA nanocomposites are discontinuous fiber composites, while HNT-PVA nanocomposites possess particulate composites structure. In addition, PVA was chemically crosslinked using different crosslinkers (glutaraldehyde, glyoxal and malonic acid) to further increase these properties as well as to control the degradation rate. Tensile, thermal, structural properties as well as waterabsorbency, solubility, crystallinity, of these polymer nanocomposites were characterized using different testing approaches to understand the role each component plays. In addition, nanomaterial dispersion was also characterized. Composting was used to test the biodegradability and characterize changes in the properties for PVA and its polymer

nanocomposites. It was observed that tensile properties of these biodegradable polymer nanocomposites were comparable or higher than many traditional plastic materials, based on theoretical calculation (rule of mixture). In addition, the synthesized polymer nanocomposites can also obtain other useful properties based on the nanomaterials' properties and resin crosslinking, including higher thermal stability and enhanced waterresistance. As a result, these nanocomposites have the potential to replace the traditional petroleum-based non-biodegradable plastic materials in many applications. The composting results also suggest that biodegradation of PVA based polymer nanocomposites in compost medium is mainly by fungal means and crystallinity, crosslinking and addition of suitable fillers can be used to control the service life of the these materials.

**Keywords**: Biodegradable materials, polyvinyl alcohol, polymer nanocomposites, nanomaterials, crosslinkers; composting

### **INTRODUCTION**

Most commercially available polymers and fiber reinforced plastics (composites) at present are non-biodegradable. Furthermore, most of them are made using petroleum as raw material, a non-renewable resource. Plastics and composites touch every part of our life. With double digit increases in the past few years in the use of plastics and composites, their waste disposal has become a serious problem [1-11]. One of the best ways to resolve these issues is to use biobased and biodegradable polymers and their composites. As a result, significant efforts are being put in developing biobased polymers and composites and the research in this field has accelerated in recent years [1-11]. Most biobased polymers derived from renewable raw materials, such as cellulose, protein and starches are inherently biodegradable [11]. However, the term 'biodegradable polymer' normally refers to synthetic polymers that decompose in natural environments, either aerobic (composting) or anaerobic (landfill) [11-13].

PVA is a widely used biocompatible thermoplastic polymer. However, unlike most petroleum based polymers, it is fully biodegradable in the presence of suitable microorganisms [1, 2, 8, 10, 11]. In addition, because of the hydroxyl (-OH) groups, PVA is strongly hydrophilic and soluble in water, which helps its degradation through hydrolysis [1, 2, 8, 10-14]. Due to its biodegradable nature, PVA nanocomposites and their crosslinked products have been widely investigated [4, 6, 7, 8, 9]. Crosslinking of PVA can increase its useful life without compromising the biodegradability. The nanofillers used in such cases include bacterial cellulose (BC), microfibrillated cellulose and halloysite nanotubes (HNT).

Bacterial nanocellulose (BC) is a promising biodegradable 'green' nanofibrous material that can be used as reinforcement in composites. BC is cellulose produced in the form of nanofibers by *Acetobacter xylinum (Acetobacter)*, a Gram-negative, obligately aerobic bacterium, in a nutritional fermentation medium at 30°C. The medium requires carbon sources and nitrogen sources, with optimum pH of 5 [4, 5, 9, 15, 16]. BC has the same chemical structure as plant-based cellulose and is produced as nanofibers with diameters between 70 and 90 nanometers. It displays many unique properties including high purity, high degree of polymerization, high crystallinity, high tensile strength and modulus and strong biological adaptability [4, 5, 9, 15-21]. The BC is already being used in many applications

including artificial skin and blood vessels, binding agent for fibers, loud speaker diaphragms, high quality paper, composite membranes, functional nanocomposites, etc. [4, 5, 9, 16, 21-26].

Microfibrillated cellulose (MFC) can be obtained by mechanical shearing of pulp cellulose fibers to small diameter fibrils through refining and high-pressure homogenization processes [6, 27-30]. Since the widths of some fibrils are in submicron range, they are considered as nanofibers [6, 27, 28, 31-33]. The MFC has high aspect ratio and high tensile properties as a result of its high molecular orientation and crystallinity. Their modulus is estimated at 140 GPa and tensile strength between 2 and 6 GPa [34].

Halloysite nanotubes (HNTs) based on aluminosilicate clay nanosheets that are naturally rolled to form hollow tubular structures are mined from natural deposits around the world [7, 35-37]. HNTs occur naturally as cylinders with average diameters typically smaller than 100 nm and lengths ranging from 500 nm to over 1.2  $\mu$ m [7, 367]. HNTs have been used as bioreactors, time-release capsules, catalysts of polymer degradation, templates for depositing other nanoparticles, polymer filler or property modifier as well as in ceramic applications [35].

Natural nanofillers may be used in PVA resin to form nanocomposites with excellent mechanical and thermal properties that can be used in many applications [5-9]. The properties of these nanocomposites can be further enhanced by crosslinking PVA with crosslinkers such as glutaraldehyde (GA), glyoxal (GX) and malonic acid (MX) [5-9].

The biodegradation mechanism of PVA and its nanocomposites have been investigated. The microorganisms capable of assimilating PVA were identified as *Pseudomonas* species [2, 8, 11, 38, 39, 40]. Further studies confirmed that other aerobic bacteria, such as *Alcaligenes* and *Bacillus*, were also active in PVA biodegradation [8,11,40-43]. Fungal strains, such as *Aspergillus niger*, *Pycnoporus cinnabarinus*, *Fusarium and Phanerochaete chrysoporium*, have also been shown to have the ability to roughen PVA surfaces and break it down [8, 11, 44, 45]. In these studies it was assumed that the initial microbial attack was consistent with the random cleavage of the polymer chains. The degradation reactions were catalyzed by specific oxidases and dehydrogenases that were isolated mainly as extracellular proteins from different bacterial species [1, 2, 8, 11, 41]. However, biodegradation of PVA is supposed to be a combinative process accomplished by many microorganisms working simultaneously [8, 40, 42-45].

PVA has been shown to degrade under different environmental conditions, including composting, soil burial, aqueous media and anaerobic conditions [8, 41, 46-49]. Composting, however, has been an effective technique to characterize the biodegradation of PVA and other biodegradable polymers and composites [2, 8]. Composting is defined as an exothermic bio-oxidative decomposition of organic materials by indigenous microorganisms in a controlled moist and warm aerobic environment leading to the production of 'compost', a mixture of water, minerals and stabilized organic matter [8, 38, 50]. As the compost pile becomes active, a succession of mesophilic and thermophilic microorganisms secrete depolymerase enzymes. These enzymes attack the substrate as nutrient in the presence of optimal moisture, temperature and nutrients [8, 38, 50]. PVA/Starch blends and their crosslinked products have been investigated and found to be fully biodegradable in compost medium [8, 51, 52]. The composting results have indicated that PVA with higher molecular weight biodegraded faster and crosslinking retarded the biodegradation [51, 52]. Biodegradation of PVA and its nanocomposites may be controlled by resin crosslinking and suitable fillers [8].

This chapter presents fabrication and characterization of PVA based polymer nanocomposites and their crosslinked products that are fully biodegradable. Their mechanical and thermal properties, biodegradation through composting and applications are also discussed. It is also shown that the biodegradation and hence their useful life can be controlled through the use of nanofillers as well as crosslinking.

### **MATERIALS AND METHODS**

### **Microorganism and Culture Media**

Acetobacter (Gluconacetobacter hansenii, ATCC 23769), obtained from the American Type Culture Collection (ATCC, Manassas, VA) was used as the model strain and maintained on agar plates containing 25 g/L D-mannitol, 5 g/L yeast extract and 5 g/L tryptone and 20 g/L agar. The mannitol culture medium used for BC production consisted of 25 g/L D-mannitol, 5 g/L yeast extract and 5 g/L tryptone [4, 5, 9, 15, 16].

### **Preparation of BC Pellicles**

The strain from the agar plate was inoculated into a conical flask containing mannitol culture medium as the seed culture. The initial pH value of the medium was adjusted to 5.0 and was not regulated during the culture. The seed culture was incubated at  $30^{\circ}$ C on a rotary shaker for 2 days at 130 rpm, and 9 mL of this seed culture was inoculated into a 150-mL culture medium in 1000-mL conical flask for production of BC. The cultivation was carried out at initial pH of 5.0 at  $30^{\circ}$ C in a static incubator for 10 days. After incubation, the BC pellicles produced on the surface of mannitol culture medium were harvested and washed successively with water and 1% (w/v), aqueous NaOH at  $90^{\circ}$ C for 15 min, and then washed with deionized water to remove all microbial product contaminants and obtain purified pellicles [4, 5, 9, 15, 16].

#### **Preparation of MFC Suspension**

MFC in water (KY-100G) was obtained from Daicel Chemical Industries, Japan. The MFC was added to deionized water at a weight ratio of 1:199. The mixture was stirred using mechanical stirrer at 80°C for 1 hr and followed by ultrasonication (Branson Ultrasonics, Model 2510, Mumbai, India) at 65°C for 1 hr to form MFC suspension and to separate the fibrils [6].

### **Individualization of HNTs**

HNT powder was initially added to deionized water at a weight ratio of 1:49. Tween<sup>®</sup> 80 (Sigma-Aldrich, St. Louis, MO) (HNT:Tween<sup>®</sup> 80 (w/w)=10:1) was then added into the

mixture, as non-ionic surfactant, to help individualize the HNTs. The pH value of the mixture was adjusted to 10 to further avoid clustering of HNTs [37]. The mixture (at pH=10) was stirred using mechanical stirrer (Polymix<sup>®</sup>, PX-SR 90 D, Kinematica Inc., Bohemia, NY) at 90°C and 1000 rpm for 1 hr and followed by ultrasonication (Branson Ultrasonics, Model 2510, Mumbai, India) at 65°C for 1 hr to form original HNT dispersion. The original HNT dispersion was kept standing for 2 days until it was stabilized. The supernatant of the HNT dispersion was used as final individualized HNT dispersion while the bottom part of the solution containing HNT deposition was removed. The HNT content in the final individualized HNT dispersion was 0.5% by wt [7].

### **Fabrication of BC-PVA Nanocomposites**

PVA powder (M<sub>w</sub> 31,000-50,000, 98-99% hydrolyzed, Aldrich, St. Louis, MO) was added to deionized water in 3.2 w/v% concentration, and the mixture was then stirred at  $80^{\circ}$ C for 30 min to form the PVA solution. The purified BC pellicles were immersed in the PVA solution and kept in a water bath maintained at 80°C for 2 hr, and were then allowed to remain in the PVA solution at room temperature for 12 hr. The PVA containing BC pellicles were then transferred into deionized water for 30 min to remove superfluous PVA on the surface of the BC pellicles to obtain BC-PVA prepregs. The BC-PVA prepregs were dried on a Teflon<sup>®</sup> plate in an oven at 45°C for 12 hr until the weights of the BC-PVA nanocomposites remained constant. The BC content in these composites was in the range of 50%. The percentage BC content was calculated on dry weight basis. The BC-PVA nanocomposites with varying BC content could be obtained, if desired, by simply adjusting the concentration of the PVA solution. BC mass was weighed after removing PVA from the BC-PVA nanocomposites by hot water washing. BC content in the composites was calculated using PVA and BC dry weights. BC and PVA were prepared by drying BC pellicles and casting PVA solution as control, for comparison. All nanocomposites, BC and PVA specimens prepared in this study were thin, membrane-like [5]. The PVA solution concentrations used and the resulting BC content obtained in BC-PVA nanocomposites are presented in Table 1.

 Table 1. BC content in BC-PVA nanocomposites. ©Springer. Reproduced by permission of Springer

Concentrations of PVA solution	BC content in
for BC pellicle treatment (w/v%)	BC-PVA nanocomposites (wt%)
1.5%	$75 \pm 4$
3.2%	$50 \pm 4$
6.0%	$25 \pm 3$

### **Fabrication of MFC-PVA Nanocomposites**

The PVA powder was added to the MFC suspension at desired weight ratios. The MFC suspension and PVA powder mixtures were stirred at 80°C for 1 hr and ultrasonicated at 65°C for 1 hr. The mixtures were cast on Teflon<sup>®</sup> glass plate and slowly dried at RT to form MFC-

PVA nanocomposites (5, 10, 15, 20, 30, 40 and 50% MFC contents (by wt) in the composites). The MFC-PVA nanocomposites were hot pressed at  $80^{\circ}$ C and 4 MPa for 30 min to form the final nanocomposites. As mentioned previously the specimen thicknesses were about 0.2 mm [6].

#### **Fabrication of HNT-PVA Nanocomposites**

The PVA solution (10% by wt) was blended with the HNT dispersion to obtain desired PVA and HNT weight ratios. The HNT dispersion and PVA solution mixtures were stirred at 90°C for 1 hr. The mixtures were cast on Teflon<sup>®</sup> coated glass plate and slowly dried in an oven at 40°C to form HNT-PVA nanocomposite sheets (5, 10 and 20 HNT loading, by wt, in the composites). The HNT-PVA nanocomposite sheets were hot pressed at 100°C under a pressure of 0.2 MPa for 60 min to form the final membrane-like nanocomposites [7].

### Fabrication of Crosslinked BC-PVA Nanocomposites

Partially crosslinked BC-PVA nanocomposites were prepared by immersion method using Glutaraldehyde (GA)-acetone solution. The BC-PVA nanocomposites with 50% BC content were initially immersed into the GA-acetone solution which contained 10% by volume GA solution (25% solution in water, Aldrich, St. Louis, MO) and 90% by volume acetone (Mallinckrodt Baker, Phillipsburg, NJ). The pH of the GA-acetone solution was adjusted to around 1.0 by hydrochloric acid to trigger the crosslinking reaction. The reason for using acetone as a solvent was to prevent the PVA from dissolving in water during the crosslinking reaction [53]. After carrying the crosslinking reaction for 12 hr at room temperature, the partially crosslinked specimens (prepregs) were taken out from the GA-acetone solution and rinsed with water to remove the residual GA and acetone. The partially crosslinked BC-PVA nanocomposites were then dried in an oven at 45°C for 12 hr until their weights stabilized [5]. Same process was used to crosslink BC and PVA specimens individually, to compare their properties.

Highly crosslinked BC-PVA nanocomposites were prepared in GA-water solution using similar method described above. The BC-PVA prepregs initially were partially dried at room temperature for 8 hr before immersing into the GA-water solution and water content in the partially dried specimens was around 50%. The partially dried BC-PVA prepregs were then immersed into the GA-water solution containing 10% by volume GA solution (25% solution in water, Aldrich, St. Louis, MO) and 90% by volume deionized water. The pH value of the GA-water solution was adjusted to around 1.0 using hydrochloric acid to trigger the crosslinking reaction. The incomplete drying of BC-PVA prepregs was to make sure the GA-water solution penetrated into the inner structures of BC-PVA prepregs and triggered the crosslinking reaction to as complete as possible. The preliminary test results had indicated that the completely dried BC lost a majority of its porous structure as the individual nanofibers stuck to each other reducing the penetration of the GA-water solution. After 12 hr of crosslinking at room temperature, the highly crosslinked BC-PVA prepregs were taken out from the GA-water solution and rinsed with deionized water to remove the residual GA. The highly crosslinked BC-PVA prepregs were taken out from the GA-water solution and rinsed with deionized water to remove the residual GA.

flatness, in an oven at 45°C for 12 hr until the weights stabilized [5]. Highly crosslinked BC specimens and highly crosslinked PVA films were also prepared using the same method to compare their properties.

### Fabrication of Crosslinked MFC-PVA Nanocomposites Using Glyoxal

The PVA powder was added to the MFC suspension at desired weight ratios. The mixtures of MFC suspension and PVA powder, at desired ratios, were stirred at 65°C for 1 hr and ultrasonicated at 65°C for 1 hr. Glyoxal solution (25 wt% solution) was then added to the MFC suspension and PVA mixture to obtain the wt ratio of glyoxal to PVA and MFC of 3:100. The pH of all mixtures were adjusted to 3 using phosphoric acid. The mixtures were stirred at 80°C for 1 hr for precuring (partial crosslinking). The precured mixtures were then cast on Teflon<sup>®</sup> coated glass plates and dried at RT to form precured crosslinked MFC-PVA nanocomposites. The precured nanocomposites were cured in an oven at 100°C for 30 min and hot pressed at 80°C and 4 MPa for 30 min to form cured (crosslinked) MFC-PVA nanocomposites. The MFC contents in crosslinked MFC-PVA nanocomposites were controlled at 5, 10, 15, 20, 30, 40 and 50% (by wt). The specimen thicknesses again were about 0.2 mm [6]. Same process was used to crosslink PVA specimens to form glyoxal crosslinked PVA, to compare their properties.

### Fabrication of Crosslinked HNT-PVA Nanocomposites Using MA

The 10% (by wt) PVA solution was added to the final individualized HNT dispersion at desired PVA and HNT weight ratios. The HNT dispersion and PVA solution mixtures were stirred at 90°C for 1 hr and ultrasonicated at 65°C for 1 hr. MA powder (ReagentPlus<sup>®</sup>, 99%, Sigma-Aldrich, St. Louis, MO) was then added to the mixtures. The weight ratio of MA to PVA was 1:10. The pH values of the mixtures were adjusted to 1 by adding crosslinking catalyst phosphoric acid (85 wt% solution in water, Mallinckrodt Baker, Phillipsburg, NJ). The mixtures were stirred at 90°C for 1 hr for precuring. The precured mixtures were then cast on Teflon<sup>®</sup> coated glass plates and slowly dried in an oven at 40°C to form flat precured crosslinked HNT-PVA nanocomposites (5, 10 and 20% HNT loading, by wt, in the nanocomposites). The precured composites were further hot pressed at 100°C under a pressure of 0.2 MPa for 60 min to form crosslinked HNT-PVA nanocomposites as stated earlier. The crosslinked HNT-PVA nanocomposites were then immersed into deionized water at RT for 12 hr until the system got stabilized in order to partially remove phosphoric acid, remaining MA and noncrosslinked PVA. The water-immersed and cured crosslinked HNT-PVA nanocomposites then dried at 40°C to form final crosslinked HNT-PVA nanocomposites with average thickness of 0.5 mm [7]. Same process was used to crosslink PVA specimens to form malonic acid crosslinked PVA, to compare their properties.

### **Composting Set-up**

Biodegradation of the specimens was characterized by composting. The composting medium was prepared by blending chicken droppings and sawdust in the ratio 1:1 (w/w) to obtain a C/N ratio of 50/50 [1-3, 8, 42].

All specimens (PVA, glyoxal crosslinked PVA, MA crosslinked PVA, MFC-PVA and HNT-PVA nanocomposites) were dried in an oven at 105°C for 12 hr and then placed in highly porous non-woven polypropylene (NPP) bags, which were then placed in the compost mix for characterizing their microbial degradation. The NPP bags facilitated easy retrieval of the buried sheet specimens and its open structure allowed moisture, air and microorganism to move in and out freely during composting. The composting conditions such as moisture, temperature, pH were monitored periodically. The moisture content of the compost mix was maintained at 50% by adding water initially and periodically. The temperature of the compost mix was maintained at 32°C (in mesophilic phase) throughout the composting. This assured that the degradation was primarily attributed to the activity of mesophilic microorganisms, actinomycetes and fungi. The pH of the compost was measured to be acidic in the range of 5.5-6.0 during composting. There is no evidence that the PVA based specimens or products can degrade themselves in this pH range. In addition, PVA solution has a low degradation rate close to this pH range by hydrolysis under ultrasonic environment [8, 44]. Composted specimens were retrieved after 30, 45, 60, 75, 90 and 120 days of composting dried in an oven at 105°C for 12 hr and characterized for various properties [1-3, 8, 42].

### Characterization

#### SEM Analysis

The specimens were sputter coated with gold and their surface topographies were observed with scanning electron microscope (SEM, LEO 1550 FESEM, Oberkochen, Germany) at an accelerating voltage of 15 kV.

#### **TEM Analysis**

HNT-PVA nanocomposites (10% HNT loading) and MA crosslinked HNT-PVA nanocomposites (10% HNT loading) were initially frozen by liquid nitrogen and then cut into thin sections (40-100 nm thickness) using microtome (Leica EM UC7/FC7 Cryoultramicrotome, Leica Microsystems, Cambridge, UK) with diamond cutter. The thin sections of HNT-PVA nanocomposites were observed with transmission electron microscopy (FEI Tecnai<sup>TM</sup> F20 TEM, FEI Company, Hillsboro, OR). Copper grids with 300 mesh size were used to hold the specimens for TEM.

#### ATR-FTIR Spectroscopy

All the specimens were characterized using a Fourier transform infrared spectrophotometer (FTIR, Nicolet Magna-IR 560, Thermo Scientific, Waltham, MA). Attenuated total reflection (ATR) FTIR spectra were taken in the range of 4000-800 cm<sup>-1</sup> wavenumbers. Each scan was an average of 64 scans obtained at a resolution of 4 cm<sup>-1</sup>. BC content in all BC-PVA nanocomposite specimens was in the range of 50% and the specimens

were dried in an oven at 45°C for 12 hr prior to the spectroscopy. Both of MFC and HNTs in their corresponding nanocomposites were in the range of 10%. Reproducibility was confirmed for each type of specimen by repeating the experiment 3 times.

#### X-ray Diffraction Studies

Wide angle X-ray diffraction (WXRD) was used to evaluate the crystallinity and/or crystal sizes of the BC, the PVA, the highly crosslinked BC and the highly crosslinked PVA that were dried in an oven at 45°C for 12 hr. The general area detection diffraction system (GADDS, Bruker-AXS, Inc., Madison, WI) was used at 45 KV and 40 mA. The X-ray diffraction patterns of all the specimens were obtained using a Scintag theta-theta powder diffractometer (PAD X, Scintag, Inc., Cupertino, CA) with a solid-state intrinsic germanium detector. All specimens were scanned from 2° to 30° at 3°/min employing the Cu K<sub>a</sub> X-ray radiation with a wavelength of 1.54 Å.

#### Tensile Property and Moisture Content Characterization

Tensile tests of various specimens were performed using an Instron tensile testing machine (Instron, model 5566, Canton, MA). All specimens were cut into 10 mm wide and 60 mm long strips using a precision cutter. Young's moduli of all specimens were determined from the tensile test results conducted according to ASTM D-882-02. Two ends of the specimens were placed between the upper and lower grips of the Instron, leaving a gauge length of 30 mm. The strain rate of 0.02/min was maintained for all specimens. All specimens were conditioned at 21°C and 65% RH for 3 days prior to tensile test.

Percent moisture content (MC%) of the conditioned specimens were measured as per ASTM D 2654-89a. To obtain the MC% values specimens were dried at 105°C until their wt stabilized.

#### TGA Analysis

Thermogravimetric analysis (TGA, TA instrument, Model No. 2050) was used to analyze the thermal properties of BC, PVA, BC-PVA nanocomposites (50% BC) and their corresponding crosslinked specimens at different levels of crosslinking. The specimens were dried in an oven at 45°C for 12 hr prior to conducting the test. All TGA analyses were performed between 25 and 600°C, and at a ramp rate of 20°C/min under a nitrogen atmosphere by maintaining a flow rate of 10 ml/min.

Thermogravimetric analysis (TGA Model Q500, TA Instrument, New Castle, DE) was used to characterize the thermal degradation behavior of all other specimens except for BC, BC-PVA and their corresponding GA crosslinked specimens. The specimens were dried in an air circulating oven at  $45^{\circ}$ C for 12 hr prior to conducting the tests. All TGA tests were performed between 25 and 800°C in a nitrogen atmosphere (flow rate of 60 ml/min) and at a scanning rate of  $10^{\circ}$ C/min.

#### DSC Analysis

Differential scanning calorimetry (DSC, Model Q2000, TA Instruments Inc., New Castle, DE) was used to analyze the glass transition temperature  $(T_g)$ , melting temperature  $(T_m)$ , enthalpy of fusion  $(\Delta H_f)$  and crystallinity of the specimens. All specimens were dried as mentioned above prior to conducting the test. All DSC tests were performed in nitrogen

atmosphere (flow rate of 50 ml/min), between -20 and 250  $^{\circ}\mathrm{C}$  and at a scanning rate of 10  $^{\circ}\mathrm{C/min}.$ 

#### Weight Loss

All control and composted specimens were dried in an air circulating oven at 105°C for 12 hr and weighed. The percent weight (wt) loss was calculated using the ratio of lost wt to original wt.

### Sol-gel Analysis of the Resins

The specimens were taken out after specific composting periods and dried prior to conducting the sol-gel test. The specimens were weighed to obtain their initial dry wt and then immersed in distilled water in 150 mL glass bottles. The glass bottles with the specimens were placed on a shaker table (MAXQ 4450, Thermo Scientific, Waltham, MA) maintained at  $80^{\circ}$ C and 150 rpm for about 2 hr or until the control (noncrosslinked) PVA was completely dissolved. The remaining solids content for the crosslinked specimens were then washed three times with distilled water and filtered using a Whatman<sup>®</sup> filter paper (Number 4, 20-25 µm pore size) to obtain final residues. The water soluble part (sol) and particles smaller than 25 µm were removed during filtration. The final residues of the crosslinked specimens were fully dried to obtain their dry wt (gel). Ratios of the gel wt of the crosslinked PVA to their corresponding initial dry wt were used as PVA gel (crosslinked) percentages. The same process was conducted for test the crosslinked effects for PVA resin and PVA based polymer nanocomposites.

#### Swelling Power Analysis

PVA and crosslinked PVA specimens (glyoxal and MA crosslinked PVA as well as crosslinked PVA resin in MFC-PVA (10% MFC) and HNT-PVA nanocomposites (10% HNT loading)) were dried at 105°C for 12 hr prior to conducting the swelling test. The specimens were weighed to obtain their initial dry wt and then immersed in distilled water in 150 mL glass bottles at RT for 24 hr. The surface water from the swollen specimens was wiped using Kimwipe<sup>®</sup> paper tissue to remove excess water weighed again to obtain the swollen wt. Ratios of the wt of absorbed water by the specimens to their corresponding initial dry wt were used to determine the swelling powers of the control and crosslinked PVA. The nanofiller (MFC and HNTs) wt in the crosslinked PVA based nanocomposites was regarded as constant, before and after the test.

#### EDX Analysis

The elemental composition of crystals observed on the surface of glyoxal and MA crosslinked PVA specimens were analyzed by energy dispersive X-ray technique (EDX, Bruker AXS Microanalysis GmbH Berlin, Germany) with primary energy of 9 KeV with 90-second scans.

### **RESULTS AND DISCUSSIONS**

### Section 1: BC-PVA Nanocomposites [5]

### 1.1. SEM Images of BC and BC-PVA Nanocomposites

Figure 1 (a and b) show the SEM images of freeze dried BC and freeze dried BC-PVA nanocomposite (50% BC) specimens, respectively. Not hot pressing the specimens can preserve their structure for observation. Figure 1 (a) shows the clear porous BC network structure of the freeze dried specimen. Diameters of 100 BC-nanofibers 100 specimens and 100 pores from SEM images indicated that the mean diameter of the BC-nanofibers was less than 100 nm and the pore diameters ranged from several dozens to several hundred nanometers. Figure 1 (b) shows excellent PVA penetration in the BC network and filling of the pores. This provides excellent opportunity to form uniform composite structures with excellent properties, when hot pressed. Similar surface topography of BC-polyethylene glycol (PEG) composites has been reported previously [44]. Structural modification can occur as the water surrounding polyglucosan chains are displaced by hydrogen bonds formed between - OH groups of BC and PEG and of BC and PVA [54-56].



Figure 1. SEM images of freeze dried BC (a) and freeze dried BC-PVA nanocomposite (b). ©Springer. Reproduced by permission of Springer.

# 1.2. ATR-FTIR Analysis of BC-PVA Nanocomposites and Crosslinked BC-PVA Nanocomposites

Figure 2 shows the ATR-FTIR spectra of the BC-PVA nanocomposites (50% BC) and BC-PVA nanocomposites crosslinked to different levels. All spectra were normalized based on bands observed at 1058 cm<sup>-1</sup> wavenumber associated with C-O stretching. ATR-FTIR spectrum 2 (a) is for the BC-PVA nanocomposite. ATR-FTIR spectrum 2 (b) is for the partially crosslinked BC-PVA nanocomposite, using the GA-acetone solution, while spectrum 2 (c) is for the highly crosslinked BC-PVA nanocomposite, using the GA-water solution. As mentioned earlier the BC content in all three specimens was around 50%. A broad band at 3200-3550 cm<sup>-1</sup>, wavenumber seen in all 3 spectra, is a result of the hydroxyl (O-H) stretching vibration resulting from the strong hydrogen bonds of intra-molecular and intermolecular type [57, 58]. The absorption band observed between 2820 and 3000 cm<sup>-1</sup> wavenumber is due to the stretching of aliphatic C-H bond [58]. Compared to spectrum 2 (a),

the absorbance intensity at 3200-3500 cm<sup>-1</sup> band in the spectrum 2 (b) is much lower. The normalized absorbance intensity ratio of bands for O-H to C-H decreased from 1.60 for spectrum 2 (a) to 1.20 for spectrum 2 (b). In the spectrum 2 (c), the absorbance intensity ratio of bands for O-H to C-H decreased even further, to 0.83. This spectral change indicates reduction in the O-H groups on the specimens as a result of crosslinking reaction with the GA [58]. Normalized absorbance of bands at 1700-1750 cm<sup>-1</sup> in the spectra 2 (a) and 2 (b) were 0.13 and 0.20 respectively. While they are not sharp, they still demonstrate the presence of carbonyl (C=O) group in the composites from the remaining non-hydrolyzed vinyl acetate group of the PVA [57, 59]. In spectrum 2 (c), however, a significantly sharp absorption (normalized absorbance of 0.57) observed at 1700-1750 cm<sup>-1</sup> wavenumber indicates stronger stretching vibration of C=O in the composites. This means that in addition to the remaining non-hydrolyzed vinyl acetate groups, some residual aldehyde groups from the GA also existed in the highly crosslinked BC-PVA nanocomposites, both combining to give stronger C=O absorption. This confirms the earlier observation that the GA-water solution can penetrate into the inner cavities of the BC-PVA nanocomposites network. Also that part of the residual GA remains trapped in the crosslinked BC-PVA nanocomposites even after wash. This is very likely when only one aldehyde group from GA reacts and the other end remains unreacted. The absorption at 1050-1150 cm<sup>-1</sup> wavenumber seen in spectrum 2 (a) is due to the presence of C-O stretching vibration from the acetate group [57-59]. The same absorption band for C-O stretching vibration was much broader in spectrum 2 (b) than in spectrum 2 (a), resulting from the formation of the acetal linkages upon reaction of the PVA with the GA. In the spectrum 2 (c), the C-O band became the broadest one in three spectra due to the high crosslinking level and the formation of more acetal linkages.



Figure 2. ATR-FTIR spectra for BC-PVA nanocomposites (a), partially crosslinked BC-PVA nanocomposites (b) and highly crosslinked BC-PVA nanocomposites (c). ©Springer. Reproduced by permission of Springer.

Overall, the ATR-FTIR results indicate that the BC-PVA nanocomposites were at the least partially crosslinked based on the decreased intensity of bands for O-H stretching and increased intensity of bands for C-O stretching. The crosslinking reactions can occur between

increased intensity of bands for C-O stretching. The crosslinking reactions can occur between hydroxyl groups of the BC, between hydroxyl groups of the PVA, or between BC and PVA. These results also confirm that a higher crosslinking level can be achieved for BC-PVA nanocomposites with GA-water solution. This is mainly because the GA-acetone solution can hardly penetrate into the fully dried BC-PVA nanocomposites, whereas the GA-water solution has the ability to penetrate the BC-PVA prepregs well. This suggests that it should be possible to control crosslinking of BC-PVA nanocomposites by controlling acetone/water ratio.

### 1.3. Sol-gel Analysis of Crosslinked PVA and BC-PVA Nanocomposites

Sol-gel analysis was performed for PVA as well as for the resin in BC-PVA nanocomposites that were crosslinked to different levels. Table 2 presents the sol-gel test results for partially and highly crosslinked PVA (the resins from BC-PVA nanocomposites) and control PVA. The results show that the gel (crosslinked) percentage of the partially crosslinked PVA was about 10%. The values were close in both the partially crosslinked PVA and the resin in the partially crosslinked BC-PVA composites BC-PVA nanocomposites. About 90% of the PVA was noncrosslinked and thus dissolved in deionized water during the sol-gel test. This indicates that the crosslinking reaction using the GA-acetone solution occurred mostly on the surfaces of the PVA and the BC-PVA nanocomposites. As mentioned earlier this was because the GA-acetone solution could not penetrate into the PVA fully to trigger the crosslinking reaction in PVA. The results also indicate that the gel (crosslinked) percentage of the highly crosslinked PVA could be over 90%. The levels of crosslinking were also close in both the highly crosslinked PVA and the resin in the highly crosslinked BC-PVA nanocomposites. While both resin and composite specimens were swollen after being in water, they remained intact. The results of this test further demonstrate that the GA-water solution was effective in crosslinking the specimens as a result of easy penetration of the PVA.

Specimens	PVA	Partially crosslinked PVA	PVA in partially cross- linked BC-PVA nanocomposites	Highly crosslinked PVA	PVA in highly crosslinked BC- PVA nanocomposites
Gel percentage in specimens (%)	0	10.8	9.6	90.2	88.9

Table 2. Sol-gel test results of PVA at different levels of crosslinking. ©Springer.Reproduced by permission of Springer

### 1.4. WXRD of BC, PVA and their Highly Crosslinked Specimens

WXRD was used to evaluate the crystallinity and the crystal sizes of the BC, the PVA and their corresponding highly crosslinked specimens. The crystallinity (%) values for individual specimens were calculated using a ratio of crystalline area to the combined crystalline and amorphous areas in the WXRD patterns [60]. The crystal sizes (d-spacing)

were calculated using the WXRD patterns using analysis software (Scintag, Inc., Cupertino, CA) based on Scherrer Equation.

Figure 3A (a) and (b) illustrate WXRD patterns obtained for BC and highly crosslinked BC, respectively. Both WXRD patterns showed distinct peaks at 20 values of  $5.5^{\circ}$ ,  $14.5^{\circ}$  and  $22.5^{\circ}$ . Figure 3A also shows that the crystallinity of the BC decreased from 62.5% (Figure 3.3A (a)) to 12.7% (Figure 3A (b)) after the crosslinking reaction. The reduction in the crystallinity is believed to be due to the crosslinking within the BC that changes the morphology and destroys the crystallites.

Figure 3B shows WXRD patterns of the control PVA (a) and highly crosslinked PVA (b). Both the WXRD patterns show a distinct peak at 2 $\theta$  values of 20°. Figure 3B indicates that the crystallinity of the PVA decreased from 61.7% (Figure 3B (a)) to 4.9% (Figure 3B (b)) after crosslinking and the average crystal size of the PVA at 20° decreased from 45 Å (Figure 3B (a)) to 14 Å (Figure 3B (b)). It should be noted that the transparency of highly crosslinked PVA was expected to be higher than the noncrosslinked PVA and confirms the reduction in crystallinity due to crosslinking. It is well understood that crosslinks restrict crystallization as well as decrease the size of the crystals by impeding the macromolecular chain folding [61, 62].



Figure 3. WXRD patterns A: BC (a) and highly crosslinked BC (b); and B: PVA (a) and highly crosslinked PVA (b). ©Springer. Reproduced by permission of Springer.

# 1.5. Tensile Properties of BC, PVA, BC-PVA Nanocomposites and their Corresponding Crosslinked Specimens

Table 3 presents the tensile test results for BC, PVA and BC-PVA nanocomposites with varying BC contents (25%, 50% and 75%). Theoretical values calculated, using the rule of mixture, for Young's modulus and fracture stress are also presented in Table 3, for comparison. The Young's modulus of the BC membrane was 3424 MPa while the Young's modulus of the PVA was 12.8 MPa. The Young's modulus values of the BC-PVA nanocomposites were between those obtained for BC and PVA as expected. With the increase in BC content, the Young's modulus of the BC-PVA nanocomposites increased as well. For composites with BC content of 25%, the Young's modulus was around 731.6 MPa and when the BC content increased to 50% and 75% the Young's modulus values increased to 1590 MPa and 2473 MPa, respectively. The fracture stress values for BC and PVA were 63.7 MPa and 5.4 MPa, respectively. It is clear that BC-PVA composite fracture stress values are between those of BC and PVA as can be expected. However, there was no direct correlation between BC content and fracture stress of the composites as was observed for the modulus values did. One reason for this is the lower fracture strain of the composites with increased

BC content. The fracture stress values ranged from 22.9 MPa for composites with BC content of 25% to 44.6 MPa when the BC content was 75%. The fracture strain of the PVA was 234.3% compared to 5.8% for BC. All fracture strains of BC-PVA nanocomposites were lower than that of BC. This is due to the extremely good bonding between PVA and BC, both with plenty of OH groups [63, 64].

Specimens	Young's	Rule of	Fracture	Rule of	Fracture
	modulus	mixture	stress	mixture	strain
	(MPa)	(MPa)	(MPa)	(MPa)	(%)
BC	3424		63.7		5.8
	(8.2)*		(50.4)		(44.7)
PVA	12.8		5.4		234.3
	(36.3)		(3.4)		(14.4)
BC-PVA	731.6	754.8	22.9	18.1	3.7
nanocomposites	(1.1)		(6.5)		(1.6)
(25% BC)					
BC-PVA	1590	1565	32.6	31.9	2.4
nanocomposites	(12.0)		(10.9)		(26.1)
(50% BC)					
BC-PVA	2473	2449	44.6	47.0	2.0
nanocomposites (75% BC)	(5.2)		(13.3)		(18.9)

# Table 3. Tensile properties for BC, PVA and BC-PVA nanocomposites with varying BC content. ©Springer. Reproduced by permission of Springer

\* Numbers in the parentheses are % coefficient of variation values.

Table 4 presents tensile test results for BC, PVA, BC-PVA nanocomposites (50% BC) and their corresponding crosslinked specimens at different crosslinking levels. The Young's modulus values of partially crosslinked BC and highly crosslinked BC increased to 4243 MPa and 5107 MPa, respectively, from 3424 MPa obtained for BC. The Young's modulus values of partially crosslinked and highly crosslinked PVA increased to 54.1 MPa and 270.1 MPa, respectively, from 12.8 MPa obtained for the control (noncrosslinked) PVA. The Young's modulus values of the partially crosslinked and highly crosslinked BC-PVA nanocomposites increased to 1875 MPa and 2429 MPa, respectively, from 1590 MPa obtained for the BC-PVA nanocomposites. While the increase in Young's modulus values is due to the crosslinked structure and increased molecular weight in the case of PVA, the crosslinking of BC makes the structure rigid when crosslinked [65]. The reduction in moisture content from 9.1% of the PVA to a lower range of 3.8-6.0% for the crosslinked specimens may also partially contribute to the increased Young's modulus. Higher crosslinking is known to result in higher modulus. From data presented in Table 4, it is clear that with increased crosslinking, all three specimens, PVA, BC and the composites, became brittle (lower fracture strain). This affects their fracture stress values and do not show a correlation to BC content as seen for Young's modulus. For example, crosslinking reduces the fracture stress of BC whereas crosslinking increases the fracture stress of PVA. And for the BC-PVA nanocomposites, there is almost no effect.

Specimens	Young's	Rule of	Fracture	Rule of	Fracture
	modulus	mixture	stress	mixture	strain
	(MPa)	(MPa)	(MPa)	(MPa)	(%)
BC	3424		63.7		5.8
	(8.2)*		(50.4)		(44.7)
Partially crosslinked BC	4243		61.6		1.9
	(14.6)		(17.5)		(27.9)
Highly crosslinked BC	5107		43.8		1.0
	(11.2)		(37.6)		(41.1)
PVA	12.8		5.4		234.3
	(36.3)		(3.4)		(14.4)
Partially crosslinked	54.1		7.9		59.6
PVA	(15.8)		(9.2)		(11.1)
Highly crosslinked	270.1		19.2		19.9
PVA	(19.6)		(5.1)		(22.9)
BC-PVA nanocomposites	1590	1565	32.6	31.9	2.4
(50% BC)	(12.0)		(10.9)		(26.1)
Partially crosslinked BC-	1875	1938	31.9	32.3	2.0
PVA nanocomposites	(15.2)		(30.4)		(34.2)
(50% BC)					
Highly crosslinked BC-	2429	2471	31.6	30.4	1.5 (39.3)
PVA nanocomposites	(4.7)		(14.3)		
(50% BC)					

Table 4. T	ensile properti	es for BC, l	PVA, BC-PV	A nanocompo	sites at different	levels of
	crosslinking.	©Springer.	Reproduced	l by permissio	on of Springer	

\* Numbers in the parentheses are % coefficient of variation values.

Tables 3 and 4 also show theoretical values for Young's modulus and fracture stress values calculated using the rule of mixture [66]. The densities of cellulose and PVA used were 1.52 g/cc and 1.27 g/cc, respectively [67], and the BC content in the BC-PVA nanocomposites varied from 25% to 75% by weight. It is interesting that the theoretical predictions and experimental values for both Young's modulus and fracture stress are very close to each other.

Figure 4 shows typical stress vs strain plots of BC-PVA nanocomposites (a) and partially (b) and highly crosslinked (c) BC-PVA nanocomposites. The BC content (by wt) in all the three specimens was around 50%. Figure 4 (a) for BC-PVA composite shows an initial elastic behavior followed by a plastic yielding. The yielding may be due to PVA's high ductility and breaking of some BC nanofibers that are in the stress direction and possible alignment of the remaining nanofibers. Once that process was over, BC-PVA nanocomposites showed elastic behavior until the fracture point. Figures 4 (b) and 4 (c) indicate no obvious yielding for partially or highly crosslinked BC-PVA nanocomposites. Once the PVA becomes crosslinked it loses its ductility. As can be expected, Figure 4 also shows that higher crosslinking level leads to higher modulus and lower fracture strain values.



Figure 4. Stress vs Strain plots for BC-PVA nanocomposites (a), partially crosslinked BC-PVA nanocomposites (b) and highly crosslinked BC-PVA nanocomposites (c). ©Springer. Reproduced by permission of Springer.

It is interesting to note that the tensile properties of BC-PVA nanocomposites and the crosslinked BC-PVA nanocomposites are close or higher than many traditional plastics, including polyethylene (Young's modulus: 800 MPa; fracture stress: 15 MPa), polypropylene (Young's modulus: 1900 MPa; fracture stress: 40 MPa), and nylon 6 (Young's modulus: 1800 MPa; fracture stress: 70 MPa) [68]. As a result, the BC-PVA nanocomposites, both crosslinked and noncrosslinked, have the potential to replace these non-biodegradable plastics in many applications such as racket frame, ski pole, circuit board, automobile inside etc. These degradable composites may be protected from water degradation by applying varnish or water-resistant coatings to increase their service life.

# 1.6. TGA of BC, PVA, BC-PVA Nanocomposites and their Corresponding Crosslinked Specimens

Figure 5A presents typical TGA thermograms of BC, partially crosslinked BC and highly crosslinked BC specimens. Thermogram 5A (a), the TGA thermogram for BC, shows the onset decomposition temperature ( $T_d$ ) at 260°C. Weight losses for BC were 30% at 284°C, 50% at 303°C and 80% at 600°C. It has been reported that two competing reaction pathways, low-temperature pathway and high-temperature pathway (>300°C), occur simultaneously during the thermal degradation of cellulose [69]. The low-temperature pathway is mainly responsible for the water loss. The primary reaction in the high-temperature pathway is depolymerization, as the cellulose structure can absorb enough energy to activate the cleavage of the glycosidic linkages to produce glucose, which is dehydrated to levoglucosan and oligosaccharides. The production of volatile compounds is complete when the temperature reaches around 450°C. The continuing weight loss is due to degradation when all other elements are driven off and the char (carbon) remains [69]. The thermogram for the BC indicates that the weight loss of cellulose is the result of a combination of both lowtemperature and high-temperature pathways. Thermogram 5A (b), for partially crosslinked BC, showed a  $T_d$  at 285°C. Weight losses for the partially crosslinked BC were 30% at 309°C, 50% at 334°C and about 83% at 600°C. Thermogram 5A (c) for highly crosslinked BC showed a T<sub>d</sub> at 315°C with weight losses of 30% at 329°C, 50% at 346°C and about 80% at

600°C. These results clearly indicate that the crosslinking makes the BC thermally more stable.

Figure 5B presents typical TGA thermograms for PVA and partially and highly crosslinked PVA. Thermogram 5B (a) for the PVA shows two decomposition onset temperatures,  $T_{d1}$  and  $T_{d2}$ , at 255°C and 400°C, respectively. Weight loss for the PVA was 50% at 279°C and up to 93% at 600°C. Two-step degradation of PVA has been reported earlier [69]. PVA first degrades into small-molecular-weight species at about 250°C and then further degrades into carbon char at temperatures above 350°C. These results confirm the findings of Peng and Kong [70]. Thermogram 5B (b) for partially crosslinked PVA shows a single  $T_d$  at 325°C. Weight losses observed were 50% at 364°C and about 97% at 600°C. Thermogram 5B (c), for highly crosslinked PVA, shows  $T_d$  at 330°C. Weight losses observed for highly crosslinked PVA were 50% at 370°C and about 97% at 600°C. The two-step degradation pattern was not so obvious for partially and highly crosslinked PVA.



Figure 5. TGA thermograms A: BC (a), partially crosslinked BC (b) and highly crosslinked BC (c); B: PVA (a), partially crosslinked PVA (b) and highly crosslinked PVA (c); C: BC-PVA nanocomposite (a), partially crosslinked BC-PVA nanocomposite (b) and highly crosslinked BC-PVA nanocomposite (c). ©Springer. Reproduced by permission of Springer.

Figure 5C shows typical TGA thermograms for BC-PVA nanocomposites and partially and highly crosslinked BC-PVA nanocomposites. As mentioned earlier BC content in all the BC-PVA nanocomposites was around 50%. Thermogram 5C (a) for BC-PVA nanocomposites shows two decomposition temperatures,  $T_{d1}$  and  $T_{d2}$  at 257°C and 380°C, respectively. Weight losses observed were 50% at 283°C and about 90% at 600°C. From thermograms for BC and BC-PVA nanocomposites, it is clear that BC reinforcement is able to increase the thermal stability of the PVA. Two distinct and well-separated degradation onsets can be seen in thermogram 5C (a) for BC-PVA nanocomposites. This degradation can also be regarded as a

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two-step-degradation and could be a result of the PVA. Thermogram for partially crosslinked BC-PVA nanocomposites presented in 5C (b) shows better thermal stability than the BC-PVA nanocomposites. The  $T_d$  for the partially crosslinked BC-PVA nanocomposites was at 307°C. Thermogram 5C (c) obtained for highly crosslinked BC-PVA nanocomposites showed the highest thermal stability among the three BC-PVA nanocomposites, as can be expected. The  $T_d$  for the highly crosslinked BC-PVA nanocomposites was 313°C and weight losses were 50% at 372°C and about 90% at 600°C. The two-step-degradation pattern was not obvious for partially and highly crosslinked BC-PVA nanocomposites.

In summary, the thermal analysis results show that crosslinking can increase the thermal stability of BC, PVA and BC-PVA nanocomposites. Other researchers have obtained similar results for soy flour, collagen and chitosan after crosslinking [71-73]. This is particularly true for highly crosslinked composites. This is in addition to their high tensile properties. The final char weights of the crosslinked specimens in TGA tests were slightly less than those of the specimens without crosslinking treatments. This is probably due to volatilization of the residual GA trapped in the crosslinked specimens during the TGA test.

### Section 2: MFC-PVA Nanocomposites [6]

### 2.1. SEM Images of MFC-PVA Nanocomposite Surface and Fracture Topographies

Figure 6 shows typical SEM images of MFC-PVA nanocomposite (noncrosslinked, 10% MFC), surface topography (A) showing MFC distribution and facture surface (B) after tensile testing. From Figure 6 (A), it can be clearly seen that the MFC fibrils are randomly organized but uniformly distributed within PVA and some of them are just at the surface of the nanocomposite. Figure 6 (B) clearly shows the MFC fibrils protruding out from the PVA at the facture surface. However, the protruding fibril lengths are very short indicating strong PVA-MFC bonding. The MFC fibrils also are distributed uniformly within the PVA at the facture surface. This is expected since both PVA and MFC have hydroxyl groups and can mix and disperse easily and also form hydrogen bonds at multiple locations. The fibrils also look oriented in the direction of the stress. This is due to the high fracture strain of the noncrosslinked composites which allows orientation during the tensile test.



Figure 6. Typical SEM images A: Surface topography of the MFC-PVA nanocomposites; B: Fracture surface of the MFC-PVA nanocomposite. Both specimens contain 10% MFC. ©Elsevier. Reproduced by permission of Elsevier.

# 2.2. ATR-FTIR Analysis of Crosslinked and Noncrosslinked MFC-PVA Nanocomposites

Figure 7A shows typical crosslinking of PVA or MFC with glyoxal. In the present case three crosslinking reactions are possible: PVA-PVA, MFC-MFC and PVA-MFC.

Figure 7B shows the ATR-FTIR spectra for control MFC-PVA nanocomposites (a) and glyoxal crosslinked MFC-PVA nanocomposites (b). A broad band at 3550-3200 cm<sup>-1</sup>, wavenumber seen in both spectra, is a result of the hydroxyl (O-H) stretching vibration resulting from the strong intra-molecular and inter-molecular hydrogen bonds [57, 58]. The absorption band observed between 3000 and 2820 cm<sup>-1</sup> wavenumbers is due to the stretching of aliphatic C-H bond [57]. The absorbance intensity ratio of bands for O-H to C-H showed a decrease from 1.81 for spectrum (a) to 1.28 for spectrum (b). This clearly indicates a reduction in the O-H groups due to crosslinking by glyoxal [58]. Absorption at 1750-1700 cm<sup>-1</sup> (stretching of C=O) for noncrosslinked specimen (spectrum (a)) was weak (intensity ratio of C=O to C-H = 0.35) and indicates the presence of carbonyl (C=O) in the composites from the non-hydrolyzed acetate groups remaining in the PVA, confirming the results obtained by Gohil et al. [57] and Mansur et al. [58]. In spectrum (b), however, a sharp absorption (intensity ratio of C=O to C-H = 0.63) observed at 1750-1700 cm<sup>-1</sup> wavenumber indicates strong presence of C=O in the crosslinked resin of the composites. This shows that in addition to the non-hydrolyzed vinyl acetate groups, some residual unreacted aldehyde groups from glyoxal also exist in the crosslinked MFC-PVA nanocomposites, both contributing to the stronger C=O absorption. Depending on the local situation glyoxal may exist as half (one group) reacted, fully reacted or unreacted. The absorption at 1150-1050 cm<sup>-1</sup> wavenumber in spectrum (a) is due to C-O stretching vibration from the acetate group [57-59]. The intensity of absorption band for C-O stretching vibration was stronger in spectrum (b) (intensity ratio of C-O to C-H = 3.38) than in spectrum (a) (intensity ratio of C-O to C-H = 2.72), resulting from the formation of the acetal linkages (shown in Figure 7A) upon reaction of the composites with the glyoxal.

In summary, the ATR-FTIR results indicate that the MFC-PVA nanocomposites were crosslinked based on the decreased intensity of bands for O-H stretching vibration combined with the increased intensity of bands for C=O and C-O stretching vibrations. As mentioned earlier, the crosslinking reactions can occur between the MFC fibrils or the PVA resin or between MFC and PVA.

#### 2.3. Sol-gel and Swelling Analyses

Sol-gel and swelling analyses were performed for noncrosslinked (control) and crosslinked PVA, as well as for the crosslinked MFC-PVA nanocomposites to evaluate the level of crosslinking. Table 5 presents sol-gel and swelling results for crosslinked PVA as well as control PVA. The results show that the PVA gel (crosslinked) percentages of the crosslinked PVA and the resin in the crosslinked MFC-PVA nanocomposites were 7.0% and 6.6%, respectively, while the control PVA dissolved completely during the sol-gel test. The low gel percentage suggests that the PVA was only partially crosslinked MFC-PVA nanocomposites were 78.3% and 75.1% respectively, much lower than control PVA (105.6%), confirming the crosslinking, though only partial.



Figure 7. A: Schematic of the acetal linkage in glyoxal crosslinked PVA or MFC structure; B: FTIR spectra of MFC-PVA nanocomposites (a: 10% MFC) and glyoxal crosslinked MFC-PVA nanocomposites (b: 10% MFC). ©Elsevier. Reproduced by permission of Elsevier.

Table 5. Sol-gel and swelling power results of PVA and glyoxal crosslinked PVA.
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Tests	PVA	Crosslinked	PVA in crosslinked
		PVA	MFC-PVA
			nanocomposites
Gel percentage (%)	0	7.0 (8.3)*	6.6 (10.3)
Swelling power (%)	105.6 (5.5)	78.3 (2.7)	75.1 (8.8)

\* Numbers in the parentheses are % coefficient of variation values.

### 2.4. Tensile Properties and Moisture Content

Table 6 presents the tensile and moisture content results for pure (control) PVA and noncrosslinked MFC-PVA nanocomposites with MFC contents from 5 to 50%. The Young's modulus of the control PVA was 248 MPa. The Young's modulus of the MFC-PVA nanocomposites were significantly higher than for PVA and increased with the MFC content, as can be expected. For composites with 5 and 10% MFC content, the Young's moduli were 687 MPa and 1033 MPa, respectively. When the MFC content increased to 50% the Young's modulus increased to 3898 MPa, about 16 times that of control PVA. This is expected since the Young's modulus for MFC is much higher [33]. The facture stress for the control PVA was

34.1 MPa. The fracture stress values for MFC-PVA nanocomposites with 5 and 10%, MFC content were 43.3 MPa and 53.5 MPa, respectively, and increased to 89.9 and 84.9 MPa when the MFC content increased to 40 and 50%, respectively. This is again because the MFC fracture stress is between 2 and 6 GPa [33]. The facture stress of MFC-PVA nanocomposites with 50% MFC, however, was lower than the composites with 40% MFC. This is because of the lower fracture strain (5.1%) of the composites with 50% MFC content compared to 8% obtained for composites with 40% MFC. Similar trend of increase in Young's modulus and fracture stress with increase in MFC content have been reported by Lu et al. [74]. While the fracture strain for control PVA was 331%, the facture strains for the MFC-PVA nanocomposites were much lower than that of PVA and decreased as the MFC content increased, as expected. The moisture content for PVA was 9.1%, and the moisture contents for MFC-PVA nanocomposites were within a narrow range of 7.1% to 8.1%. This is because moisture contents of MFC and PVA are very close.

Table 6. Tensile properties for MFC-PVA nanocomposites with varying MFC content
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Weight percentage of MFC content in MFC-PVA composites	Young's modulus (MPa)	Fracture stress (MPa)	Fracture strain (%)	Moisture content (%)
0 (PVA)	248 (22.9)	34.1 (13.3)	331 (15.4)	9.1 (4.2)
5	687 (10.3)	43.3 (4.6)	34.7 (13.4)	7.7 (5.5)
10	1033 (7.2)	53.5 (5.6)	25.2 (23.7)	7.4 (11.8)
15	1399 (13.6)	65.0 (8.0)	18.3(12.1)	7.3 (25.1)
20	1707 (8.0)	69.6 (8.3)	15.2 (12.4)	8.0 (1.0)
30	2538 (10.7)	81.6 (7.7)	8.9 (18.8)	8.1 (2.9)
40	3409 (9.4)	89.9 (13.5)	8.0 (26.2)	7.1 (12.6)
50	3898 (21.3)	84.9 (11.9)	5.1 (31.7)	7.7 (20.3)

\* Numbers in the parentheses are % coefficient of variation values.

Table 7 presents tensile and moisture content results for PVA, MFC-PVA nanocomposites (10% MFC) and their corresponding glyoxal crosslinked specimens. The Young's moduli of the crosslinked PVA and crosslinked MFC-PVA nanocomposites increased to 666 MPa and 1404 MPa, from 248 MPa for control PVA and 1033 MPa for noncrosslinked MFC-PVA nanocomposites, respectively. It is obvious that the increase in Young's modulus for the PVA and MFC-PVA nanocomposites is due to the crosslinking of the PVA which makes the structure rigid [65]. In the case of the MFC-PVA nanocomposites, not only the PVA is crosslinked but the MFC fibrils can also get crosslinked between themselves as well as with PVA. The reduction in moisture content from 9.1% for the PVA to 5.5% after crosslinking and from 7.4% for the MFC-PVA nanocomposites to 7.3% for the crosslinked MFC-PVA nanocomposites is also responsible, at least partially, for higher Young's modulus. From data in Table 7, it is also clear that after crosslinking, PVA fracture strain is significantly lower. However, MFC-PVA nanocomposites fracture strains did not change after crosslinking since this property is controlled by the MFC. While crosslinking increased the PVA fracture stress from 34.1 MPa to 47.7 MPa, MFC-PVA nanocomposites showed no significant change. This

is because the crosslinked composites showed sharp yielding. And after the yielding, the stress remained the same. As a result, no change in the fracture stress was observed. Similar effect has also been observed in the case of bacterial cellulose reinforced PVA composites [5].

Specimens	Young's modulus (MPa)	Fracture stress (MPa)	Fracture strain (%)	Moisture content (%)
PVA	248 (22.9)	34.1 (13.3)	331 (15.4)	9.1 (4.2)
Crosslinked PVA	666 (9.5)	47.7 (7.5)	184(16.3)	5.5 (28.5)
MFC-PVA	1033 (7.2)	53.2 (5.6)	25.2 (23.7)	7.4 (11.8)
(10 wt% MFC content)				
Crosslinked MFC-PVA	1404 (9.4)	53.7 (7.1)	29.6 (16.8)	7.3 (1.7)
(10 wt% MFC content)				

Table 7. Tensile properties for PVA, MFC-PVA nanocomposites and their glyoxal crosslinked specimens. ©Elsevier. Reproduced by permission of Elsevier

\* Numbers in the parentheses are % coefficient of variation values.

It should be noted that as in the case of BC-PVA composite tensile properties of MFC-PVA nanocomposites and crosslinked MFC-PVA nanocomposites are also higher than many traditional polymers, including polyethylene, polypropylene and nylon 6 [68]. In addition, fabrication process for the biodegradable MFC-PVA nanocomposites is convenient and simple and the cost for raw materials is low. Therefore, both crosslinked and noncrosslinked MFC-PVA nanocomposites have the potential to replace traditional non-biodegradable plastic materials in many applications as discussed for BC-PVA nanocomposites. The moisture sensitivity of these composites is reduced after crosslinking, making them more useful. Further, they can be easily protected from water by applying varnish or water-resistant coatings, thus increasing their service life.

### 2.5. Thermogravimetric Analysis

Figure 8A shows TGA thermograms of PVA, MFC-PVA nanocomposites (10% and 40% MFC) and MFC. Thermogram 8A (a) for control PVA shows two decomposition onset temperatures,  $(T_{d1})$  and  $(T_{d2})$ , at 257°C and 400°C, respectively. Weight losses for the PVA were 50% at 281°C and up to 94% at 800°C. Two-step-decomposition of PVA has been reported earlier and is discussed in section 1.6 [70]. Thermograms 8A (b) and 8A (c) for MFC-PVA nanocomposites with 10 and 40% MFC, respectively, also show two decomposition temperatures, corresponding to PVA decomposition. Weight losses observed for the MFC-PVA nanocomposites (10% MFC) were 50% at 288°C and 92% at 800°C. Weight losses observed for the MFC-PVA nanocomposites (40% MFC) were 30% at 285°C, 50% at 313°C (both temperatures higher than those obtained for MFC-PVA nanocomposites with 10% MFC) and 92% at 800°C. Thermogram 8A (d) for MFC showed a single decomposition onset temperature ( $T_d$ ) at 315°C. Weight losses observed for pure MFC were 50% at 340°C and 85% at 800°C, indicating higher thermal stability than PVA and close to the values obtained by Quiévy et al. [75]. These results confirm that, as in the case of BC, MFC reinforcement is responsible for the higher thermal stability of the MFC-PVA nanocomposites and supports earlier results by Lu et al. [74].

Figure 8B presents typical TGA thermograms of PVA, MFC-PVA nanocomposites (10% MFC) and their corresponding glyoxal crosslinked specimens. Thermograms 8B (a) and 8B (b) are for PVA and MFC-PVA nanocomposites, respectively, and have been described in the last paragraph. Thermogram 7B (c), for crosslinked PVA, also shows a two-step degradation pattern with  $T_{d1}$  and  $T_{d2}$  observed at 370°C and 410°C, respectively. However, the steps are not as distinct compared to the control PVA. The weight losses observed were 50% at 368°C and 91% at 800°C. These temperatures are significantly higher than those obtained for control PVA confirming that the crosslinked PVA has significantly higher thermal stability as is the case for many polymers [71-73]. Similarly thermogram 8B (d) for crosslinked MFC-PVA nanocomposites also shows a two-step degradation pattern with  $T_{d1}$  and  $T_{d2}$  observed at 300°C. As is expected these values are close to those obtained for the crosslinked PVA, the major constituent. These results confirm that glyoxal crosslinking increases the thermal stability of PVA and the MFC-PVA nanocomposites in addition to enhancing their tensile properties.



Figure 8. TGA thermograms A: PVA (a), MFC-PVA nanocomposites (b: 10% MFC), MFC-PVA nanocomposites (c: 40% MFC) and MFC (d); B: PVA (a), MFC-PVA nanocomposites (b: 10% MFC), glyoxal crosslinked PVA (c) and glyoxal crosslinked MFC-PVA nanocomposites (d: 10% MFC). ©Elsevier. Reproduced by permission of Elsevier.

#### 2.6. Differential Scanning Calorimetry

Typical DSC thermograms for PVA and glyoxal crosslinked PVA are presented in Figure 9A. Thermogram 9A (a) shows  $T_g$  and  $T_m$  of 92.1°C and 195.4°C, respectively, for PVA. The  $\Delta H_f$  of 86.9 J/g, compared to 138.6 J/g for 100% crystalline PVA resulted in a crystallinity of 62.7% for control PVA [66, 76-78]. Thermogram 9A (b) for the crosslinked PVA shows  $T_g$  and  $T_m$  of 110°C and 175.4°C, respectively. The  $\Delta H_f$  and the crystallinity of the crosslinked PVA were 55.3 J/g and 39.9%, respectively. The lower  $\Delta H_f$  and higher  $T_g$  further confirm that the PVA was partially crosslinked by glyoxal. The higher  $T_g$  and lower crystallinity after crosslinking due to restricted segmental motion, have been observed in most polymers [60-62, 66].

Figure 9B presents typical DSC thermograms of (a) MFC-PVA nanocomposites and (b) glyoxal crosslinked MFC-PVA nanocomposites. The  $T_g$  and  $T_m$  for the MFC-PVA nanocomposites were observed at 92.0°C and 197.5°C, respectively. These values are close to those obtained for PVA. While the  $T_g$  of cellulose is around 230°C, MFC is highly crystalline and hence does not show any  $T_g$ . Also, no  $T_m$  for cellulose can be observed since it degrades

prior to melting [79, 80]. As a result, the DSC thermogram primarily corresponds to PVA. The conclusion here is in agreement with the phenomenon observed by Lu et al. [74]. The  $\Delta H_f$  and the crystallinity of the PVA in MFC-PVA nanocomposites were 61.4 J/g and 44.3%, respectively, which were much lower than 86.9 J/g and 62.7%, respectively, obtained for control PVA. It is likely that the well dispersed nano- and micro-fibrils in the MFC can inhibit the PVA crystallization. The fibrils can suppress the free movement of polymeric chains restricting their ability to fold and thus lower the crystallinity [81]. Thermogram 9B (b) is for crosslinked MFC-PVA nanocomposites but, as discussed earlier, mainly corresponds to crosslinked PVA. The Tg and Tm observed at 110.2°C and 178.8°C, respectively, reconfirm that glyoxal crosslinking can increase  $T_g$ , decrease the  $T_m$  of PVA. These changed characteristics are reflected in the crosslinked MFC-PVA nanocomposites. The  $\Delta H_f$  and crystallinity of PVA in crosslinked MFC-PVA nanocomposites were 50.5 J/g and 36.4%, respectively. These are lower than the PVA in MFC-PVA nanocomposites and slightly lower than those for the crosslinked PVA, showing the combined effect of crosslinking and the ability of the MFC to restrain the molecular motion needed for crystallization.



Figure 9. DSC thermograms A: PVA (a) and glyoxal crosslinked PVA (b); B: MFC-PVA nanocomposites (a: 10% MFC) and glyoxal crosslinked MFC-PVA nanocomposites (b: 10% MFC). ©Elsevier. Reproduced by permission of Elsevier.

### Section 3: HNT-PVA Nanocomposites [7]

### 3.1. HNT Individualization

The HNT used in this research was in the raw form and contained nanotube clusters. Same separation techniques were employed to individualize HNT clusters as discussed earlier. These techniques include: high speed mechanical stirring, ultrasonication, addition of non-ionic surfactant and changing the solution pH. Non-ionic surfactant Tween<sup>®</sup> 80 was used as a dispersant to improve the HNT separation or individualization [82].

It has been reported that at pH 7.5 and above, the HNTs tend to repel each other since the charge on both the edge and face surface is negative [83]. As a result, the system deflocculates and loses cohesion. Uniform and stable HNT dispersion was obtained after using these separation techniques sequentially, as discussed in section titled 'Individualization of HNTs'. This stable HNT dispersion was used to prepare HNT-PVA nanocomposites.

### 3.2. Mechanism of Uniform HNT Dispersion in Acidic Crosslinking Condition

The individualized HNTs in dispersion can aggregate and deposit when the solution pH is changed to acidic. However, after HNT dispersion was mixed with PVA solution, the aggregation did not occur for many days, even in acidic condition, during PVA crosslinking. This may be because of the high viscosity of the PVA solution which prevents them from coming closer due to the change of charges on edge surfaces of the HNTs in acidic environment. The surface of HNTs may be even wrapped by polymers. Earlier research has shown that polyaniline does wrap around HNTs. Silicone oil with polyaniline-wrapped HNTs dispersed in it was shown to have electrorheological properties [84]. Figure 10 shows a schematic of this mechanism. It shows individualized HNTs can aggregate with each other in acidic situation. However, as mentioned earlier, high viscosity of PVA solution can help individualized HNTs to retard or even prevent aggregation by immobilizing them.



Figure 10. HNT clustering (a) and PVA surrounded HNTs without clustering (b) in acidic environment. ©John Wiley & Sons. Reproduced by permission of John Wiley & Sons.



Figure 11. TEM images of HNT-PVA nanocomposite (a) and crosslinked HNT-PVA nanocomposite (b) Both contain 10% HNT loading. ©John Wiley & Sons. Reproduced by permission of John Wiley & Sons.

### 3.3. TEM and SEM Analysis of HNT Dispersion in PVA and Crosslinked PVA

Figure 11 shows typical TEM images of (a) HNT-PVA nanocomposite and (b) MA crosslinked HNT-PVA nanocomposite thin sections. All nanocomposites had 10% HNT loading. Both TEM images clearly show that the HNTs were individualized and the uniformly dispersed within the PVA or crosslinked PVA. As mentioned earlier high viscosity of the PVA solution helps reduce individualized HNT aggregation by immobilizing them. The degree or

uniformity of dispersion of the HNTs within the polymer plays an important role on its mechanical properties [85]. Also, since the HNTs are uniformly dispersed, both mechanical and thermal properties of the nanocomposites would also be expected to be uniform [37].

#### 3.4. Sol-gel and Swelling Analyses

A study of crosslinking of PVA with dicarboxylic acids, including MA, with sulfuric acid as a catalyst has been described earlier [86]. Since our preliminary results showed no difference in the extent of crosslinking between MA crosslinked PVA catalyzed by sulfuric acid and phosphoric acid, for all subsequent experiments phosphoric acid was used as a catalyst to crosslink PVA and HNT-PVA nanocomposites because of its lower toxicity compared to sulfuric acid [87].

Sol-gel and swelling analyses can be used to evaluate the level of crosslinking. Table 8 presents the sol-gel and swelling results for MA crosslinked PVA as well as control PVA. The results show that gel (crosslinked component) percentages of the crosslinked PVA and the resin in the crosslinked HNT-PVA nanocomposites were 93.1% and 94.8%, respectively, while the control PVA dissolved completely during the sol-gel test. The high gel percentage suggests that the PVA was crosslinked by MA when catalyzed by phosphoric acid. The results also show that the swelling powers of crosslinked PVA and the resin in the crosslinked HNT-PVA nanocomposites were 52.3% and 51.0%, respectively, much lower than control (noncrosslinked) PVA (107.3%), further confirming the crosslinking.

Tests	Control PVA	Crosslinked PVA	PVA in crosslinked HNT-PVA** nanocomposites
Gel percentage (%)	0	93.1 (8.3)*	94.8 (7.2)
Swelling power (%)	107.3 (5.2)	52.3 (9.2)	51.0 (8.0)

 Table 8. Sol-gel and swelling power results of PVA and MA crosslinked PVA. ©John

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\* Numbers in the parentheses are % coefficient of variation.

\*\* 10% HNT.

### 3.5. ATR-FTIR Analysis

When MA is made to react with PVA, the carboxylic groups (COOH) in MA react with the hydroxyl groups (OH) in the PVA forming ester linkages. Figure 12A shows typical carboxylic ester linkages in MA crosslinked PVA. Figure 12B shows (a) ATR-FTIR spectra for control HNT-PVA nanocomposite and (b) MA crosslinked HNT-PVA nanocomposite. Since HNTs cannot crosslink with MA, ATR-FTIR spectra only indicate the chemical changes within the PVA resin in HNT-PVA nanocomposites before and after crosslinking. A broad band at 3500-3200 cm<sup>-1</sup> wavenumber seen in both spectra is a result of the O-H stretching vibration resulting from the strong intra-molecular and inter-molecular hydrogen bonding [57-59]. The absorption band observed between 3000 and 2820 cm<sup>-1</sup> wavenumbers is due to the stretching of aliphatic C-H bonds [58]. The absorbance intensity ratio for O-H to C-H bands showed a decrease from 1.82 in spectrum (a) for control PVA compared to 1.23 for spectrum (b) for crosslinked PVA. This lower absorption clearly indicates a reduction in the O-H groups and confirms the crosslinking of PVA by MA [57]. Absorption at 1750-1650 cm<sup>-1</sup>

(stretching of C=O) for noncrosslinked specimen (spectrum (a)) was weak (intensity ratio of C=O to C-H = 0.50) and indicates the presence of carbonyl (C=O) in the nanocomposites from the nonhydrolyzed acetate group remaining in the PVA (98-99% hydrolyzed), confirming the earlier results obtained by Gohil et al. [57] and Mansur et al. [58]. In the ATR-FTIR spectrum (b), however, a slightly sharp absorption (intensity ratio of C=O to C-H = 0.61) observed at 1750-1650 cm<sup>-1</sup> wavenumber indicates presence of C=O in the crosslinked PVA of the nanocomposites as expected. This shows that in addition to the nonhydrolyzed vinyl acetate groups, some residual unreacted carboxylic groups from MA and carboxylic ester groups (shown in Figure 12A) from crosslinked PVA also exist in the crosslinked HNT-PVA nanocomposites, both contributing to the stronger C=O absorption.



Figure 12. A: Schematic of the carboxylic ester linkage in MA crosslinked PVA structure; B: ATR-FTIR spectra of HNT-PVA nanocomposite (a) and MA crosslinked HNT-PVA nanocomposite (b). Both contain 10% HNT loading. ©John Wiley & Sons. Reproduced by permission of John Wiley & Sons.

Overall, the ATR-FTIR results indicate that the PVA in HNT-PVA nanocomposites were crosslinked based on the decreased intensity of bands for O-H stretching vibration combined with the increased intensity of bands for C=O stretching vibrations. This confirms other results as well.

#### 3.6. Tensile Properties and Moisture Content

Table 9 presents tensile test results and moisture content values for pure (control) PVA and noncrosslinked HNT-PVA nanocomposites with HNT loading from 5 to 20% and their MA crosslinked specimens. The Young's modulus for the control PVA was 245 MPa. The Young's modulus for the HNT-PVA nanocomposites were higher than that obtained for control PVA and increased with the HNT loading, as was expected. For nanocomposites with 5 and 10% HNT loading, the Young's moduli were 286 MPa and 388 MPa, respectively, and when the HNT loading increased to 20% the Young's modulus increased to 466 MPa, about 2 times that of control PVA. This phenomenon is commonly observed for most polymers loaded with inorganic nanoparticles due to the increased tortuosity of the polymer molecules, significantly harder nanoparticles and increased nanoparticle-polymer interface [60, 88-93]. The facture stress for the control PVA was 34.3 MPa. The fracture stresses for HNT-PVA nanocomposites with 5 and 10% HNT loading were 29.1 MPa and 27.7 MPa, respectively, and decreased to 22.0 MPa when the HNT loading increased to 20%, respectively. This is attributed to the significantly reduced fracture strain resulting from HNT agglomeration in some areas of the nanocomposites, again, a phenomenon seen in most polymers. However, lower fracture strain may also be a result of the weaker bonds between the nanoparticles (HNTs) and PVA as noted by other researchers [94]. The fracture strain for control PVA was 336%. As seen from data in Table 2, fracture strains for the HNT-PVA nanocomposites are much lower than that obtained for control PVA and decreased as the HNT loading increased. The reduced fracture strain as a function of nanoparticle loading has been observed by many for other polymer nanocomposites [90]. The moisture content for control PVA was 9.2%, whereas for HNT-PVA nanocomposites with 5, 10 and 20% HNT loading the moisture content values were 8.0, 7.4 and 6.6%, respectively. This is because moisture content of HNTs is only around 1.6%, lower than PVA.

The Young's moduli of the MA crosslinked PVA and MA crosslinked HNT-PVA nanocomposites with 5, 10 and 20% HNT loading increased to 1023 MPa, 1105 MPa, 1185 MPa and 1244 MPa, respectively, from 245 MPa for control PVA and from 286 MPa, 388 MPa and 466 MPa for noncrosslinked HNT-PVA nanocomposites with same HNT loading. It is obvious that the increase in Young's modulus for the crosslinked PVA and HNT-PVA nanocomposites is solely due to the crosslinking of PVA which makes it rigid [65]. The reduction in moisture content from 9.2% for the noncrosslinked PVA to 6.3% after crosslinking and from 8.0%, 7.4% and 6.6% for the noncrosslinked HNT-PVA nanocomposites with 5, 10 and 20% HNT loading, respectively, to 6.2%, 6.0% and 6.0% for the crosslinked HNT-PVA nanocomposites with the corresponding HNT loading is also responsible, at least partially, for higher Young's modulus. With lower moisture content, i.e., less plasticization, the structure maintains its higher rigidity or stiffness [95]. Crosslinking also increased fracture stress values of PVA from 34.3 MPa to 46.4 MPa. For HNT-PVA nanocomposites with 5, 10 and 20% HNT loading the fracture stress values increased from 29.1 MPa, 27.7 MPa and 22.0 MPa to 42.1 MPa, 38.8 MPa and 36.1 MPa, respectively, after crosslinking. From data presented in Table 9, it is also clear that after crosslinking, fracture strains of PVA and HNT-PVA nanocomposites are significantly lower, as expected [88, 89, 96, 97]. The fracture strains, particularly in the case of crosslinked nanocomposites decreased significantly with HNT loading. The decrease in fracture stress is closely related to the decreased fracture strains.

Specimens	Young's modulus	Fracture	Fracture	Moisture content
	(MPa)	stress	strain	(%)
		(MPa)	(%)	
PVA	245 (20.6)*	34.3 (13.6)	336 (10.1)	9.2 (5.3)
Crosslinked PVA	1023 (19.1)	46.4 (8.5)	186 (30.2)	6.3 (7.6)
HNT-PVA	286 (16.2)	29.1 (8.7)	297 (32.1)	8.0 (5.6)
(5% HNTs)				
HNT-PVA	388 (17.0)	27.7 (9.8)	268 (22.9)	7.4 (1.0)
(10% HNTs)				
HNT-PVA	466 (11.3)	22.0 (10.7)	159 (34.8)	6.6 (1.0)
(20% HNTs)				
Crosslinked HNT-PVA	1105 (10.4)	42.1(9.5)	110 (22.3)	6.2 (4.2)
(5% HNTs)				
Crosslinked HNT-PVA	1185 (24.7)	38.8 (9.6)	74.9 (17.6)	6.0 (8.8)
(10% HNTs)				
Crosslinked HNT-PVA	1244 (0.4)	36.1 (0.6)	8.8 (22.9)	6.0 (6.1)
(20% HNTs)				

Table 9. Tensile properties and moisture content for PVA, HNT-PVA nanocomposites and their corresponding MA crosslinked specimens. ©John Wiley & Sons. Reproduced by permission of John Wiley & Sons

\* Numbers in the parentheses are % coefficient of variation values.

It should be noted that tensile properties of noncrosslinked HNT-PVA and crosslinked HNT-PVA nanocomposites are comparable or higher than many traditional polymers, including polyethylene, polypropylene and nylon 6 [68]. As a result, these PVA based biodegradable nanocomposites could easily be used in place of these traditional plastics. Also, after crosslinking their moisture sensitivity decreases, making them more useful. Biodegradable plastics based on PVA can reduce the current landfilling load significantly.



Figure 13. Typical stress vs strain plots for noncrosslinked HNT-PVA nanocomposite (a) and MA crosslinked HNT-PVA nanocomposite (b). Both contain 10% HNT loading. ©John Wiley & Sons. Reproduced by permission of John Wiley & Sons.

Figure 13 shows typical stress vs strain plots of (a) noncrosslinked HNT-PVA nanocomposite and (b) MA crosslinked HNT-PVA nanocomposite. The HNT loading in both specimens was 10% by wt. Figure 13 (a) shows HNT-PVA nanocomposite initially showed elastic behavior but then showed a plastic plateau (yielding) until reaching its fracture point. This plateau is due to PVA's high ductility that the HNTs with low aspect ratio cannot alter. While stress vs strain plot for the crosslinked HNT-PVA nanocomposite shown in Figure 13 (b) also shows yielding, it shows no plateau for plastic deformation because of the low-ductility of the crosslinked PVA.

### 3.7. Thermogravimetric Analysis

Figure 14A presents typical TGA thermograms of PVA, HNT-PVA nanocomposites (10% and 20% HNT loading) and HNTs. Thermogram 14A (a) for control PVA shows two decomposition onset temperatures,  $(T_{d1})$  and  $(T_{d2})$ , at 255°C and 390°C, respectively. Weight losses for the PVA were 50% at 276°C and up to 94% at 800°C. Two-step degradation of PVA has been discussed earlier and has been observed by others [70]. Thermograms 14A (b) and 14 A (c) for HNT-PVA nanocomposites, with 10 and 20% HNT loading also show two decomposition onset temperatures corresponding to PVA. However, their  $T_{d1}$  and  $T_{d2}$  at 260°C and 393°C, respectively, are 3 to 5°C higher than those observed for PVA. While the differences are small, they still confirm the higher thermal stability due to the addition of HNTs. Weight losses observed for the HNT-PVA nanocomposites (10% HNT loading) were 50% at 305°C and 88% at 800°C. Weight losses observed for the HNT-PVA nanocomposites (20% HNT loading) were 50% at 343°C (higher than that obtained for HNT-PVA nanocomposites with 10% HNT loading) and 74% at 800°C. Thermogram 14A (d) for HNTs showed no sharp thermal degradation. Weight losses observed for pure HNTs were 10% at 471°C, 20% at 700°C, and 24% at 800°C, confirming higher thermal stability of HNTs [98]. All these results suggest that HNT loading improves the thermal stability of the HNT-PVA nanocomposites.

Figure 14B presents typical TGA thermograms of PVA, HNT-PVA nanocomposite (10% HNT loading) and their corresponding MA crosslinked specimens. Thermograms 14B (a) and 14B (b) for PVA and HNT-PVA nanocomposites, respectively, have been described in the last paragraph. Thermogram 14B (c), for crosslinked PVA, also shows a two-step degradation pattern with  $T_{d1}$  and  $T_{d2}$  (not so obvious) observed at 305°C and 417°C, respectively. However, the steps are not as distinct when compared to the control PVA. The weight losses observed were 50% at 362°C and almost 100% at 800°C. These results indicate that the crosslinked PVA has significantly higher thermal stability compared to control PVA in the range of 240-430°C. Increased thermal stability after crosslinking has been observed earlier for many polymers [71-73]. It was also observed that the final residual percentage for MA crosslinked PVA was lower than pure PVA. This is partially because of the unreacted crosslinker (MA) and catalyst (phosphoric acid) that remain trapped in the HNT-PVA nanocomposites. During the TGA test these compounds are removed at a relatively lower temperature. Thermogram 14B (d) for crosslinked HNT-PVA nanocomposites also shows a single step degradation with  $T_d$  observed at 380°C. Weight losses observed were 30% at 329°C, 50% at 372°C and 86% at 800°C. As is expected these values are close to those obtained for the crosslinked PVA, the major constituent in the nanocomposite. These results clearly indicate that crosslinking of PVA using MA can increase its thermal stability as well as that of HNT-PVA nanocomposites in addition to enhancing their tensile properties.



Figure 14. Typical TGA thermograms A: PVA (a), HNT-PVA nanocomposite (b: 10% HNT loading), HNT-PVA nanocomposite (c: 20% HNT loading) and HNTs (d); B: PVA (a), HNT-PVA nanocomposite (b: 10% HNT loading), MA crosslinked PVA (c) and MA crosslinked HNT-PVA nanocomposite (d: 10% HNT loading). ©John Wiley & Sons. Reproduced by permission of John Wiley & Sons.

#### 3.8. Differential Scanning Calorimetry

Typical DSC thermograms for PVA and MA crosslinked PVA are presented in Figure 15A. Thermogram 15A (a) for control PVA shows  $T_g$  and  $T_m$  of 92.0°C and 196.1°C, respectively. The  $\Delta H_f$  of 81.1 J/g, compared to 138.6 J/g for 100% crystalline PVA resulted in a crystallinity of 58.5% for control (pure) PVA [66, 76-78]. Thermogram 15A (b) for the crosslinked PVA shows  $T_g$  and  $T_m$  of 102.1°C and 189.7°C, respectively. The  $\Delta H_f$  and the crystallinity of the crosslinked PVA were 36.8 J/g and 26.6%, respectively. The lower  $\Delta H_f$  and higher  $T_g$  further confirm that the PVA was effectively crosslinked by MA. The higher  $T_g$  and lower crystallinity after crosslinking are due to restricted segmental motion of the molecules and are commonly observed phenomena in most polymers [60-62, 67].

Figure 15B presents typical DSC thermograms of (a) HNT-PVA nanocomposite and (b) MA crosslinked HNT-PVA nanocomposite. The  $T_g$  and  $T_m$  for the HNT-PVA nanocomposites were observed at 90.5°C and 201.9°C, respectively. The change in  $T_g$  for nanocomposite is insignificant. While the  $T_m$  value is about 5°C higher than that of control PVA, the  $T_g$  is about 1.5°C lower. This suggests that HNTs can decrease  $T_g$  and increase  $T_m$  of polymers [99, 100].

Nakamura et al. [101] also observed similar decrease in Tg as a result of HNT addition. They argued that this was a result of free volume addition. The  $\Delta H_f$  and the crystallinity of the PVA in HNT-PVA nanocomposites (10% loading) were 43.3 J/g and 31.2%, respectively, which were much lower than 85.9 J/g and 62.0%, respectively, obtained for control PVA. It is likely that the HNTs can inhibit the crystallization of PVA, as they are well dispersed [81]. However, higher  $T_m$  suggested that the average crystal size in nanocomposites was larger. Thermogram 15B (b) is for MA crosslinked HNT-PVA composites but mainly represents crosslinked PVA behavior. The  $T_g$  and  $T_m$  observed were 99.0°C and 191.9°C, respectively, and confirm earlier observations that MA crosslinking can increase  $T_g$  and decrease  $T_m$  of PVA. These changed characteristics are reflected in the crosslinked HNT-PVA nanocomposites. The  $\Delta H_f$  and crystallinity of PVA in crosslinked HNT-PVA nanocomposites were 8.6 J/g and 6.2%, respectively. These are significantly lower than those for the PVA in HNT-PVA nanocomposites and the MA crosslinked PVA, showing the combined effect of crosslinking and the ability of the HNTs to restrain the molecular motion needed for crystallization.



Figure 15. DSC thermograms A: PVA (a) and MA crosslinked PVA (b); B: HNT-PVA nanocomposite (a) and MA crosslinked HNT-PVA nanocomposite (b). Both contain 10% HNT loading. ©John Wiley & Sons. Reproduced by permission of John Wiley & Sons.

### Section 4: Biodegradation of PVA Based Nanocomposites [8]

#### 4.1. Surface Characterization (SEM and EDX) during Degradation

Typical SEM photomicrographs showing surface characteristics of PVA (control), glyoxal crosslinked PVA (GX-PVA, in section 4), MA crosslinked PVA (MX-PVA, in section 4) and MFC-PVA (10 wt% MFC content) and HNT-PVA nanocomposites (10 wt% HNTs loading) as a function of composting days are presented in Figures 15, 16, 17, 18 and 19, respectively.

As can be seen in Figure 16 (A), the control PVA specimens had relatively smooth surfaces. After 30 days of composting no significant difference was observed in surface topography (Figure 16 (B)). However, some traces were seen on the surface after 45 days of composting (Figure 16 (C)). These traces, branched filamentous structures, are known as fungal hyphae [102, 103]. In most fungi, hyphae are the main mode of vegetative growth. These are commonly generated during composting if the temperature is suitable for the mesophilic phase as suggested by earlier studies [102, 103]. The number of fungal hyphae on the resin increased after 60 and 75 days of composting shown in (Figure 16 (D)) and (Figure 16 (E)), respectively, with some crisscrossing each other. Some grooves along with more fungal hyphae were observed on the surfaces of PVA specimens after 90 days of composting indicating deeper biodegradation of the specimens (Figure 16 (F)). Fungal hyphae and deeper cracks spread everywhere on the surface of PVA specimen and resulted in specimens breaking down into small pieces after 120 days of composting (Figure 16 (G)). Similar results were observed earlier for poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) during its biodegradation [37].

In the case of crosslinked GX-PVA specimens, a different sequence of biodegradation was observed. The control GX-PVA specimens showed smooth surface as before (Figure 17 (A)). After 30 days of composting, surface of the resin began to get rougher and showed a layer with crystal-like elements (Figure 17 (B)). These crystals were assumed to be formed by the residual catalyst phosphoric acid that leached out and crystalized during composting [104]. The presence of residual phosphoric acid and possibly its salts on the surface of the specimen were confirmed using energy-dispersive X-ray (EDX) analysis. A typical EDX spectrum showing a strong peak for phosphorous at 2 KeV (Energy axis) is presented in Figure 21. Other two strong peaks seen in Figure 21 are for oxygen at 0.5 KeV and sodium at 1.1 KeV respectively. The sodium peak is thought to be from sodium salts commonly present in the chicken manure [105]. After 45 days of composting, both surface roughness of the resin and the thickness of the crystal layer increased (Figure 17 (C)). However, the size of crystals was unchanged. The crystalline structure of the layer became even more obvious on the surface of the resin after 60 days (Figure 17 (D)) and the crystal layer spread all over the surface along with some grooves after 75 days of composting (Figure 17 (E)). After 90 days, deeper grooves were seen indicating significant biodegradation of GX-PVA (Figure 17 (F)). The specimen broke down into many small pieces at the end of 120 days of composting (Figure 17 (G)). Fungal hyphae were not seen on GX-PVA surfaces during composting. However, it is possible that they may have been covered by the thick crystalline or salt layer.

The crosslinked (control) MX-PVA specimens also showed smooth surfaces (Figure 18 (A)). After 30 and 45 days of composting, no obvious changes except some small crystals, from leached residual phosphoric acid, were seen on their surfaces (Figure 18 (B) and 18 (C)). After 60 days, more crystals were seen on the specimen surfaces (Figure 18 (D)). However, the amount of residual phosphoric acid was less on the surface of MX-PVA than on the surface of GX-PVA since less phosphoric acid was used for preparing MX-PVA specimens. MA helped lower the pH to 1 used for crosslinking. In addition, the MA crosslinked specimens were treated by water to phosphoric acid, at least partially, after crosslinking. After 75 days, many fungal hyphae appeared on the specimen surfaces (Figure 18 (F)). Deep cracks were also seen on the surface and the specimen broke into small pieces after 120 days of composting suggesting high extent of biodegradation of MX-PVA (Figure 18 (G)).

Figure 19 (A) shows the MFC-PVA nanocomposite specimen surface where MFC fibrils are randomly organized but uniformly distributed. It is assumed that the MFC fibrils are uniformly distributed within the MFC-PVA nanocomposite as well. After 30 days of composting, no significant difference can be seen in the nanocomposite surface (Figure 19 (B)). However, some fungal hyphae were observed on the surface of the nanocomposite after 45 days (Figure 19 (C)). The number of fungal hyphae increased after 60 days (Figure 19 (D)) and some finer grooves appeared on the surfaces after 75 days of composting (Figure 19 (E)). After 90 days, the grooves became larger and deeper resulting in the specimen breaking into fragments (Figure 19 (F)). The specimens composted for 120 days showed deeper cracks and were picked up as pieces (Figure 18 (G)).

The control HNT-PVA nanocomposites (Figure 20 (A)) also had smooth surfaces. After 30 days of composting, no obvious change was observed on their surfaces (Figure 20 (B)) and only a few spots and a few cracks were seen after 45 days of composting (Figure 20 (C)). Fungal hyphae were observed only after 60 days of composting (Figure 20 (D)) which increased significantly after 75 days of composting (Figure 20 (E)). After 90 days deeper grooves were seen which lead the specimen breaking up (Figure 20 (F)). Deeper cracks appeared after 120 days of composting the specimens were seen to break into pieces (Figure 20 (G)).

In summary, the SEM results indicated that the fungi played an important role during biodegradation of the PVA based materials. The fungal hyphae were seen to begin after 30 days of composting and spread over the surface of all PVA based specimens and initiating the degradation during composting [45, 46]. With additional composting time, surface roughness of specimens increased, especially after 75 days. While the roughness is an important factor that facilitates the specimens breaking into pieces, it also expedites the biodegradation rate by providing additional surface for the fungi to attack. Crosslinking (GX and MX) and filler addition (MFC and HNT), to some extent, decreased the biodegradation rate of the PVA materials and can be used increase the life of a product, if needed.



Figure 16. SEM photomicrographs showing the surface characteristics of PVA specimens as a function of composting time. ©Springer. Reproduced by permission of Springer.



Figure 17. SEM photomicrographs showing the surface characteristics of GX-PVA specimens as a function of composting time. ©Springer. Reproduced by permission of Springer.



Figure 18. SEM photomicrographs showing the surface characteristics of MX-PVA specimens as a function of composting time. ©Springer. Reproduced by permission of Springer.



120 days

Figure 19. SEM photomicrographs showing the surface characteristics of MFC-PVA nanocomposites (10 wt% MFC content) as a function of composting time. ©Springer. Reproduced by permission of Springer.



120 days

Figure 20. SEM photomicrographs showing the surface characteristics of HNT-PVA nanocomposites (10 wt% HNTs loading) as a function of composting time. ©Springer. Reproduced by permission of Springer.



Figure 21. EDX spectrum showing elements in crystals on the surface of GX-PVA and MX-PVA specimens after composting. ©Springer. Reproduced by permission of Springer.

#### 4.2. Weight Loss during Composting

The effect of composting time on the weight loss of the PVA, GX-PVA, MX-PVA and MFC-PVA and HNT-PVA nanocomposite specimens is presented in Figure 22. The data indicate that the weight loss for PVA specimen was 0.2, 2.1, 2.7, 3.2, 5.2 and 20.1% after 30, 45, 60, 75, 90 and 120 days of composting, respectively. While the weight loss was small (0.2%) during the first 30 days of composting, it accelerated between 90 and 120 days (15%) and specimens also broke into small pieces. Such rapid weight loss after 90 days of composting confirms the results obtained by other researchers [10]. Crosslinked GX-PVA specimens, however, showed a relatively higher weight loss, 3.2% in the first 30 days of composting. This was primarily due to the leaching of residual catalyst phosphoric acid in the resin. Once the phosphoric acid was leached out the rate of weight loss of GX-PVA specimens decreased and was slightly lower than control PVA specimens, although the total weight loss was higher. For example, the weight loss between 30 and 45 days of composting was only 0.3%. After 120 days, the weight loss of GX-PVA specimens only reached to 15.1%, lower than over 20% observed for control PVA specimens. The real weight loss, considering about 3% loss of phosphoric acid, is only about 12%. This suggests that glyoxal crosslinking, though only partial, can decrease biodegradation rate. Reduced degradation rate of polymers after crosslinking has been reported [6, 106, 107]. The weight loss for MX-PVA specimens reached 0.8% after 30 days of composting. This was higher than that for PVA specimens due to the leaching out of residual catalyst phosphoric acid in the resin. However, much lower amount of phosphoric acid was used in the case of MX-PVA specimens. Once the phosphoric acid leached out, the weight loss (biodegradation) rate of MX-PVA specimens decreased and was lower than both control PVA and GX-PVA specimens. Weight losses for MX-PVA specimens were much smaller. This lower biodegradation is because MA is a better crosslinking agent compared to glyoxal and results in higher crosslinking [6, 7, 106]. This conclusion was further confirmed by sol-gel results which are described later. For MFC-PVA

and HNT-PVA nanocomposites, the initial weight losses were close to those of PVA specimens, about 0.1% after 30 days of composting. However, the nanocomposites lost less weight than PVA thereafter. These results contradict with some of the previous reports suggesting that addition of dispersed phase can increase the biodegradation rate of polymers [108-111]. However, in the present case, it is because the dispersed phase, MFC, is highly crystalline and provides crack-bridging that delays breaking apart of the PVA film. In the case of HNTs they themselves do not degrade and influence the process during composting. From Figure 22, sharp increase in weight losses can be observed for all specimens from 75 to 120 days of composting confirming the SEM results of specimen breaking in that period. The increased surface roughness provides additional surface for the fungi to act and, thus, may also expedite the biodegradation to some extent.



Figure 22. Effect of composting time on the weight loss (%) of PVA, GX-PVA, MX-PVA, MFC-PVA nanocomposite and HNT-PVA nanocomposite. ©Springer. Reproduced by permission of Springer.

#### 4.3. ATR-FTIR Spectroscopy

The effect of composting time on the PVA specimen surface chemistry analyzed using ATR-FTIR and is presented in Figure 23, where spectra (a), (b) and (c) represent PVA specimens after 0, 60 and 120 days of composting, respectively. A broad band at 3500-3200 cm<sup>-1</sup> wavenumber (O-H stretching) can be seen in all three and results from the intra- and inter-molecular hydrogen bonding in PVA [57-59]. The absorption between 3000 and 2820 cm<sup>-1</sup> wavenumbers is from the aliphatic C-H bonds [57]. The absorbance intensity ratio of O-H to C-H bands showed a decrease from 1.81 in spectrum (a) for control PVA specimen compared to 1.32 for spectrum (b) (60 days of composting) and 1.11 for spectrum (c) (120 days of composting). The lower ratio clearly indicates a reduction in the O-H groups and confirms degradation of PVA with composting as explained by Chiellini et al. [9]. Absorption at 1750-1600 cm<sup>-1</sup> (stretching of C=O) for PVA before composting (spectrum (a)) was weak (intensity ratio of C=O to C-H = 0.51) and indicates the presence of carbonyl (C=O) in the resin from the nonhydrolyzed acetate group remaining in the PVA, confirming earlier results by Gohil et al. [57] and Mansur et al. [58]. In the ATR-FTIR spectrum (b), however, a slightly sharper absorption (intensity ratio of C=O to C-H = 0.55) observed at 1750-1600  $\text{cm}^{-1}$ indicates presence of more C=O in the PVA after 60 days of composting. This confirms PVA

biodegradation that results in the formation of  $\beta$ -hydroxylketone and 1, 3-diketone groups by a random cleavage of the polymer chains catalyzed by the enzymes [11, 42, 43]. In the ATR-FTIR spectrum (c), a much higher absorption (intensity ratio of C=O to C-H = 1.13) observed at 1750-1600 cm<sup>-1</sup> wavenumber indicates presence of many more C=O groups in PVA after 120 days of composting. This is expected due to continued biodegradation with composting time. These results also indicate formation of ketone groups during composting based on the decreased absorption intensity for O-H stretching vibration combined with the increased intensity of bands for C=O stretching vibrations.



Figure 23. ATR-FTIR spectra of PVA after 0 days (a), 60 days (b) and 120 days (c) of composting. ©Springer. Reproduced by permission of Springer.

The effect of composting time on GX-PVA specimen surface chemistry by ATR-FTIR is presented in Figure 24, in which spectra (a), (b) and (c) representing GX-PVA after 0, 60 and 120 days of composting, respectively, are shown. Two broad bands at 3500-3200 cm<sup>-1</sup> and 3000-2820 cm<sup>-1</sup> wavenumber are due to O-H stretching and aliphatic C-H stretching, respectively [57-59]. For spectrum (a), the two bands are well separated, and the absorbance intensity ratio of bands for O-H to C-H is 1.28, which is lower than that obtained for pure PVA due to crosslinking of the O-H groups. However, for spectra (b) and (c), no obvious separation is seen. This is primarily because of the leaching out of the phosphoric acid (catalyst) and crosslinker (glyoxal) during composting. In addition, the absorbance intensity ratio of O-H to C-H bands decreased to 1.11 and 0.87, respectively, for spectra (b) and (c). The lower absorption indicating a reduction in the O-H groups confirms degradation of PVA with composting time. Absorption at 1750-1600 cm<sup>-1</sup> (stretching of C=O) for control GX-PVA (spectrum (a)) was weak (intensity ratio of C=O to C-H = 0.63) and indicates the presence of carbonyl (C=O) in the specimens from residual unreacted aldehyde groups from glyoxal and the nonhydrolyzed acetate groups in PVA. In the ATR-FTIR spectra (b), however, a much sharper absorption (intensity ratio of C=O to C-H = 1.09) observed at 1750-1600 cm<sup>-1</sup> wavenumber indicates presence of higher number of C=O groups in the GX-PVA after 60 days composting. This increase in intensity is due to the ketone groups obtained from the

biodegradation of GX-PVA [1, 2, 11, 41]. In the ATR-FTIR spectrum (c), the intensity ratio of C=O to C-H observed at 1750-1600 cm<sup>-1</sup> wavenumber is 1.08, almost similar with that in spectrum (b). Glyoxal has been reported as a biodegradable chemical and can degrade during composting [107]. Therefore, more ketone groups generated from degrading GX-PVA helped to maintain the intensity of C=O in spectrum (c).



Figure 24. ATR-FTIR spectra of GX-PVA after 0 days (a), 60 days (b) and 120 days (c) of composting. ©Springer. Reproduced by permission of Springer.

The effect of composting time on MX-PVA specimen surface chemistry by ATR-FTIR is presented in Figure 25, where spectra (a), (b) and (c) represent MX-PVA specimens after 0, 60 and 120 days of composting, respectively. As seen in spectra (a), (b) and (c), during composting, the absorbance intensity ratio (O-H to C-H) showed a decrease from 1.42 in spectrum (a) for control MX-PVA to 1.37 for specimens after 60 days of composting (b) and 1.22 for specimens after 120 days of composting (c). The lower ration confirms degradation of MX-PVA at the surface with composting. Absorption at 1750-1600 cm<sup>-1</sup> (stretching of C=O) for MX-PVA before composting (spectrum (a)) was relatively weak (intensity ratio of C=O to C-H = 0.46) and indicates the presence of carbonyl (C=O) in the resin from residual MA and the nonhydrolyzed acetate group in PVA [57, 58]. In the ATR-FTIR spectrum (b), however, a slightly sharper absorption (intensity ratio of C=O to C-H = 0.50) observed at 1750-1600 cm<sup>-1</sup> indicates presence of higher number of C=O groups in the MX-PVA after 60 days composting. This confirms the formation of  $\beta$ -hydroxylketone and 1, 3-diketone groups by a random cleavage of the polymer chains as shown by other researchers [11, 42, 43]. In the ATR-FTIR spectrum (c), a sharper absorption observed at 1750-1600 cm<sup>-1</sup> indicates presence of higher number of C=O groups in the MX-PVA after 120 days of composting suggesting that higher number of ketone groups are created as the degradation proceeds with composting time. In summary, the MX-PVA specimens also degrade during composting but the change is not as significant as pure PVA or GX-PVA, due to higher crosslinking.



Figure 25. ATR-FTIR spectra of MX-PVA after 0 days (a), 60 days (b) and 120 days (c) of composting. ©Springer. Reproduced by permission of Springer.

The effects of composting time on the MFC-PVA and HNT-PVA nanocomposites were identical to pure with PVA based on ATR-FTIR spectra where only PVA degraded leaving MFC and HNT intact, within the 120 days of composting.

#### 4.4. DSC Study

The melting temperatures  $(T_m)$ , enthalpies  $(\Delta H_f)$  of fusion and crystallinity values observed in DSC scans for control and crosslinked PVA based resins and nanocomposites as a function of composting time are presented in Table 10. It is interesting to note that both  $T_m$ and  $\Delta H_f$  for all specimens, including PVA, GX-PVA, MX-PVA, MFC-PVA and HNT-PVA nanocomposite specimens increased with composting time during the initial 45 days. The crystallinity values for all the specimens were calculated based on 138.6 J/g for 100% crystalline PVA [66, 76-78]. After 45 days of composting,  $T_m$  and crystallinity increased from 196.1°C and 44.8% to 210.1°C and 53.6%, respectively, for PVA, from 175.6°C and 39.9% to 200.8°C and 49.5% for GX-PVA, from 188.2°C and 33.8% to 193°C and 50.0% for MX-PVA, from 198.6°C and 37.2% to 208.3°C and 50.4% for MFC-PVA nanocomposites and from 199.7°C and 40.0 to 210.1°C and 47.6% for HNT-PVA nanocomposites. Two factors are responsible for the increase of crystallinity. The first factor, as mentioned earlier, is that the microbes (fungi) attack the amorphous domain first and digest it away. As the amorphous fraction decreases, the percent crystallinity in the remaining resin increases [3]. In addition, hydrolytic degradation also occurs primarily in the amorphous regions contributing to increased crystallinity [2, 3, 112, 113]. Similar increase in crystallinity was observed for polyester fibers and soy protein isolate films earlier [2, 3, 76, 77]. The second factor is that the oligomeric PVA species in the amorphous regions acquire more chain mobility during composting, because of the absorbed moisture enabling them get incorporated into the existing crystals [112-114]. This process, involving an increase in the density due to higher

crystallinity, is called chemicrystallization [112-114]. This process also increases  $T_m$  and  $\Delta H_f$  values as seen by others [112-114]. Changes in  $T_m$  and  $\Delta H_f$  values for all the specimens were less significant between 45 and 75 days of composting. However, they increased quickly between the 75 days to 90 days of composting. This indicates that more amorphous PVA biodegraded and was incorporated into existing crystals during this period. This was confirmed from the SEM and weight loss observations. However, both  $T_m$  and  $\Delta H_f$  for all the specimens remained constant or even slightly decreased between 90 days to 120 days of composting, even though all specimens degraded significantly. It is very likely that both enzymes and moisture started affecting both crystalline and amorphous regions simultaneously [115].

Composting time	PVA	GX-PVA	MX-PVA	MFC-PVA	HNT-PVA nanocomposite
(Days)/Tiopentes				(10% MFC)	(10% HNTs)
$0/T_{\rm m}$ (°C)	196.1	175.6	188.2	198.6	199.7
Enthalpy (J/g)	62.1	55.3	46.9	51.6	55.4
Crystallinity (%)	44.8	39.9	33.8	37.2	40.0
30/T (°C)	206.9	199.2	192.4	204.8	208.2
Enthalpy (J/g)	68.6	64.6	47.9	58.1	61.2
Crystallinity (%)	49.5	46.6	34.6	41.9	44.3
45/T <sub>m</sub> (°C)	210.1	200.8	193.0	208.3	210.1
Enthalpy $(I/\sigma)$	74 3	68.6	50.0	69.8	66.0
Crystallinity (%)	53.6	49.5	36.1	50.4	47.6
60/T (°C)	210.8	199.2	192 7	209.9	211.7
Enthalpy $(I/\sigma)$	210.0 76.6	70.3	50.1	70.0	66 5
Crystallinity (%)	55.3	50.7	36.1	50.5	48.0
75/T., (°C)	210.6	202.4	193 1	210.6	211.4
Enthalny $(I/\sigma)$	210.0 76.8	69.7	50.4	68.4	65.6
Crystallinity (%)	55.4	50.3	36.4	49.4	47.3
90/T (°C)	212.5	205.9	194.0	211.5	213.0
Enthalny $(I/g)$	81.0	74.1	54 7	72.0	69.8
Crystallinity (%)	58.4	53.5	39.0	51.9	50.4
$120/T_{\rm m}$ (°C)	211.8	205.3	195.0	211.0	212.6
Enthalpy (J/g)	81.4	72.8	54.3	71.1	69.4
Crystallinity (%)	58.7	52.5	39.2	51.3	50.1

Table 10. Effect of composting time on the melting temperature and melting enthalpy of PVA based resins and nanocomposites. ©Springer. Reproduced by permission of Springer

Based on the results presented in Table 10 and results obtained in our previous research, following conclusions may be made [6, 7]. After glyoxal and MA crosslinking, the  $T_m$ ,  $\Delta H_f$ and crystallinity values decreased. Lower  $\Delta H_f$  and crystallinity values after crosslinking are quite common for many polymers as they cannot crystallize [6, 7, 60-62, 107]. The  $T_m$  for the MFC-PVA nanocomposite (198.6°C) was close to that obtained for PVA. No  $T_m$  for cellulose can be observed as it degrades prior to melting [79, 80]. As a result, the DSC thermogram mainly represented the PVA behavior. The  $\Delta H_f$  and the crystallinity of the PVA in MFC-PVA nanocomposites were 51.6 J/g and 37.2%, respectively, which were much lower than 62.1 J/g and 44.8%, respectively, obtained for control PVA. It is likely that the well dispersed nano- and micro-fibrils in the MFC inhibit the crystallization of PVA. The fibrils can suppress polymeric chain movement restricting their ability to fold and thus lower the crystallinity [81]. The  $T_m$  for the HNT-PVA nanocomposite (199.7°C) was 3.6°C higher than that of control PVA. This suggests that HNTs have the ability to lead to slightly increased  $T_m$ of polymers [7, 100, 116]. The  $\Delta H_f$  (55.4 J/g) and the crystallinity (40%) of the PVA in HNT-PVA nanocomposite (10% loading), however, were much lower than 62.1 J/g and 44.8%, respectively, obtained for control PVA.

#### 4.5. Sol-gel Analysis

The gel percentages for PVA, GX-PVA and MX-PVA specimens as a function of composting times are presented in Table 11. As seen in Table 11, the gel percentage before and during composting was 0%, for the control PVA specimens. However, in the case of crosslinked GX-PVA, the gel percentage increased from 7.0% to 7.5% after 30 days of composting. This initial increase in gel percentage is due to the preferential leaching out of the noncrosslinked part during the first 30 days of composting. Thereafter, gel percentages of the specimen decreased and reached 4.6% and 4.4% after 90 days and 120 days of composting respectively. This indicates that composting process can break crosslinks and reduce the gel percentage was similar. After 30 days of composting, the gel percentage remained unchanged. Thereafter, gel percentages of the specimen decreased only slightly to 87.9% after 120 days of composting. Slow cleavage/breakage of crosslinks and, hence, slower degradation may be used advantageously to increase the life of the resin or the nanocomposite.

Common estimate times	DVA	CV DVA	MV DVA
Composing time	PVA	GA-PVA	MA-PVA
(Days)			
0	0	7.0	90.3
30	0	7.5	90.5
45	0	4.9	89.1
60	0	4.9	88.6
75	0	5.0	88.5
90	0	4.6	88.5
120	0	4.4	87.9

# Table 11. Effect of composting time on the gel (%) of PVA, GX-PVA and MX-PVA.©Springer. Reproduced by permission of Springer

### CONCLUSION

Biodegradable polyvinyl alcohol (PVA) was utilized as resin along with different nanomaterials to fabricate biodegradable nanocomposites in the present study. Their properties, biodegradation mechanisms and applications were investigated. Nanomaterials, including fully biodegradable bacterial cellulose (BC) and microfibrillated cellulose (MFC) and naturally occurring halloysite nanotubes (HNTs) were uniformly dispersed in PVA to fabricate biodegradable polymer nanocomposites. BC-PVA nanocomposites are continuous fiber composites, MFC-PVA nanocomposites are discontinuous fiber composites, while HNT-PVA nanocomposites possess particulate composites structure. Chemical crosslinking using different crosslinkers (glutaraldehyde (GA), glyoxal and malonic acid (MA)) was carried out to further increase these properties. Tensile, thermal, structural properties as well as water-absorbency, solubility, crystallinity, of these polymer nanocomposites were characterized using different testing approaches to understand the role each component plays. In addition, nanomaterial dispersion was also been characterized. Composting was used to test the biodegradability and characterize changes in the properties for PVA and its based polymer nanocomposites.

The results indicate that tensile properties of the PVA based biodegradable nanocomposites were comparable or higher than many traditional plastic materials based on theoretical calculation (rule of mixture). In addition, the synthesized polymer nanocomposites can also obtain other useful properties based on the nanomaterials' properties and resin crosslinking, including higher thermal stability and enhanced water resistance. As a result, these nanocomposites have the potential to replace these traditional non-biodegradable plastic materials in many applications, including racket frame (tennis, badminton, etc.), ski pole, circuit board, automobile inside, etc. The compositing results also suggest that biodegradation of PVA based nanocomposites in compost medium is mainly by fungal means. Importantly, the results showed that the PVA based nanocomposite biodegradation can be controlled through the judicious use of crosslinking and fillers. This can allow fine tuning their service life depending on the application.

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