

Article

Thermal, Mechanical and Morphological Properties of Cellulose/Lignin Nanocomposites

Mustafa Zor ^{1,2}, Ferhat Şen ^{1,*} , Hikmet Yazıcı ³ and Zeki Candan ^{2,4} 

¹ Department of Nanotechnology Engineering, Zonguldak Bülent Ecevit University, 67100 Zonguldak, Türkiye; mustafa.zor@beun.edu.tr

² Biomaterials and Nanotechnology Research Group & BioNanoTeam, 34473 Istanbul, Türkiye; zekic@istanbul.edu.tr

³ Department of Design, Caycuma Vocational School, Zonguldak Bülent Ecevit University, 67900 Zonguldak, Türkiye; hikmet.yazici@beun.edu.tr

⁴ Department of Forest Industrial Engineering, Istanbul University—Cerrahpasa, 34473 Istanbul, Türkiye

* Correspondence: ferhatsen@beun.edu.tr

Abstract: Lignin, a lignocellulosic polymer material, is an important active ingredient for the high-value use of renewable resources. Thus, policies for the recovery and high value-added use of renewable lignocellulosic biomass are a realistic engineering approach to address concerns such as the climate and energy crisis. In this work, the mechanical properties, thermal stability and morphology of cellulose/lignin nanocomposites were studied. Nanocomposite films containing different proportions of lignin (2.5%, 5%, 10% and 20%) were prepared. Thermal properties were assessed via thermogravimetric analysis and differential scanning calorimetry, mechanical properties via tensile test and morphological properties via scanning electron microscopy techniques. It was observed that nanolignin and nanocellulose structures are compatible with each other and depending on the main degradation temperature, the thermal stability of 2.5% lignin-containing nanocomposites is higher than that of other composites. From the results obtained, it was determined that the nanocomposite film containing 2.5% nanolignin had high thermal stability, mechanical strength and suitable morphological structure compared to other samples.

Keywords: nanocellulose; nanolignin; composite films; characterization



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1. Introduction

In recent years, it has been observed that some technologies have been proposed for the preparation of biomaterials based on natural origin polymers containing nanometric cellulose, and to produce functional and advanced materials. Cellulose is the most common natural polymer due to its low density, high aspect ratio, high surface area and excellent mechanical properties [1]. On the other hand, lignin is a biopolymer that is naturally the largest source of aromatic compounds and is considered a waste material or energy source, especially in the pulp and paper industry. Producing thermoset material from this raw material for use in composite applications has become the preferred way in recent years. With the rapid development of nanotechnology over the last 20 years, nanocellulose, which is preferred in food, textile, paint or pharmaceutical applications, is preferred both at the level of biocompatible materials and nanostructure with its effective physical structure and strong surface chemistry [2]. It has been used in many application areas, such as medical sciences, surface functionalization, nanocomposites and adaptability, coating film and photonics, and more which continue to be investigated [3–6].

Nanocellulose, which is one of the most popular green materials of modern times due to its renewability, abundance in nature and chemical properties, is obtained from biomass, bacteria or plants based on simple scalable and isolation techniques. Cellulose polymer of natural origin is purified via nanocellulose extraction; it consists of a complex engineering

product consisting of mechanical, chemical and enzymatic processes or a combination thereof. This product has excellent thermal stability and mechanical properties and a high Young's modulus, biocompatibility and readjustability. A wide variety of nanomaterials and nanocomposites are included in the production of nanocellulose, including nanocellulose, carbon-based polymers, metals, and metal oxides. Moreover, it is used in the production of organic-based materials, where it imparts its mechanical properties to the composite [7].

The stable distribution of nanocellulose in polymer matrices improves the healing effect of the composites, and the surface properties and interface compatibility of nanocellulose are also very important in terms of application performance. Since it is an engineering material with unique properties such as high elastic module, high specific surface area, optical transparency, low thermal expansion, nano-scalability and biocompatibility, it can be used in many engineering fields due to its biodegradable features [8–13].

Mingyan et al. [14] fabricated lignin-containing cellulose nanofibrils (LNCFs) from wheat straw, using a p-toluene sulphonic acid hydrotrope combined with ultrasonication. A 5% wt of polyvinyl alcohol (PVA) was added to the obtained cellulose nanofibrils. Field emission scanning electron microscopy, atomic force microscopy and transmission electron microscopy were used to describe the morphological and structural properties of the lignin-containing cellulose nanofibrils obtained. Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) were used to investigate the variations in functional groups and the crystallization degree of the samples. Thermal stability, mechanical performance and surface hydrophobicity of the films were also investigated.

Du et al. [15] developed flexible packaging materials using 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)-oxidized cellulose nanoparticles as additives to adjust the rheology of water-based acrylic resin coatings. They prepared three different cellulose nanoparticles (cellulose nanofibers, microcrystalline cellulose and cellulose nanocrystals) with a diameter of 20 nm to 20 μ m and a length of 234 nm to 500 nm, oxidized the surfaces of the nanoparticles and integrated the carboxyl groups. Thus, they reported that nanoparticles increase their zeta potential and improved the stability of cellulose nanoparticles in water-based acrylic resin coatings.

Tang et al. [16] analyzed the chemical components of cellulose, hemicellulose and lignin of five different leaf species (pine needles, black acacia leaves, bamboo leaves, elm leaves and poplar leaves). Analyses were performed via scanning electron microscope, FT-IR, scanning electron microscopic (SEM) and XRD using the bio-enzymatic method to prepare cellulose nanoparticles from these five types of leaves. From the results, it was observed that the hemicellulose contents of bamboo leaves were the highest, while the lignin contents were the highest in the other four leaf species. According to thermal, morphological and XRD analyses, it has been proven that cellulose nanoparticles obtained from leaf species form a three-dimensional network structure and nanometer levels are clearly visible in scanning electron microscopy. The study reveals the fact that the use of leaf species can be expanded into a high value-added product. Tozluoğlu et al. [17] produced and characterized nanofibrillated and microfibrillated cellulose using both kraft pulp and NaBH₄-modified kraft pulp produced from the red gum tree. They reported that their products have high thermal stability, and nanofibril celluloses have higher dynamic mechanical properties. Zhang et al. [18] used cellulose nanocrystals and cellulose nanofibers to improve the poor elongation at break (~3%) of polyhydroxybutyrate. They reported that the elongation at break and Young's modulus increased by 91.2% and 18.4%, respectively, with a 1% amount added. Sertkaya et al. [19] investigated the chemical, morphological, thermal and rheological properties of nanocellulose obtained after different enzymatic pretreatments applied to pulp fibers bleached with soda-NaBH₄ of wheat straw. In the results, chemical analysis was performed after enzymatic pretreatment; SEM images taken after homogenization under high pressure proved that the fibers were homogeneously reduced to nano size in nanocellulose production.

Today, alternative innovative solutions to the environmentally negative effects of plastic production in terms of human health have been pursued due to the increasing global demand for non-fossil energy resources. The demand for cost-effective eco-friendly green materials continues to advance in terms of waste management and reducing pollution problems in industry. For this reason, the intense interest in sustainable biomaterials has made rational approaches to solving these problems a more viable interest both in academic studies and by industrial organizations. Although a large number of synthetic polymers are used in industry, the need to integrate them into different industrial applications seems to be making progress even in the field of natural polymers. In recent years, significant progress has been made in obtaining lignin biopolymers from sustainable and natural sources, especially in bio-based degradable natural polymers based on this source. Especially in academia and industrial organizations, efforts to transform petroleum-based materials into sustainable, environmentally friendly green materials draw attention as an important activity at present. Therefore, importance is given to the development of lignin-based biodegradable engineering materials with thermomechanical performance that can compete with these materials.

Lignin is used as a high-performance substitute raw material in the preparation of chemical products and polymers, as well as having a well-defined partially flexible structure chemically [20]. Lignin, which is the second most abundant biopolymer on earth after cellulose, is an engineering product used in many fields such as industrial and medical applications, hybrid composites, agricultural and agricultural applications, medicine, drug systems, textiles and cosmetics. It is a natural polymer that has been among the green composites developed in the last ten years and is open to development due to its high surface area and pores and striking carbon structure when used as nanolignin [21]. Due to its lignin structure, its surface is easier to change than that of macro/micro lignin since it contains a significant number of functional groups. Therefore, the preparation of lignin-based nanoparticles is of interest to researchers for various value-added applications [22,23]. Wide applications of lignin as a reinforcing material in the production of biocomposite materials and bio-based products obtained without structural degradation of lignin are greatly preferred in the sector. However, due to some negative by-products, it is not possible to fully produce high value-added applications of lignin [24,25]. The diversity of lignin sources and the complexity of their structure are also reported to present certain opportunities and challenges in research into potential applications of these materials. Therefore, different perspectives are sought to produce lignin-based nanomaterials, further expanding the high value-added applications of lignin [26,27].

Brianna et al. [28] presented a review of the methods developed to synthesize lignin, monolignols and polymers produced from lignin-derived chemicals. The majority of commercial plastics and materials used in the industry are seen as various high value-added carbon-containing engineering materials such as lignocellulosic biomass and biofuels as the most readily available and edible form of carbon, from which petroleum-based chemicals are obtained, showing strong dependence on products from non-renewable energy sources.

Nanolignin materials are highly prone to agglomeration due to the high surface energy of nanoparticles and the Van DerWalls forces between many hydrogen-bond molecules. The main problem here is to completely solve nanoparticle aggregation and to obtain monodispersion of nanolignin. In addition, it is reported that a prerequisite for the use of lignin in high value-added and very harsh areas is diversified morphology of the nanoparticles and the size effect. To eliminate the interface and dispersion problem of nanolignin materials, it is very important to determine the correct chemical method in changing the structure of nanolignin and to determine effective physical dispersion methods such as mechanical mixing, ultrasonication and high shear homogenization [29].

Makri et al. [30] prepared and characterized poly(lactic acid)/lignin composites. They reported that the tensile strength and Young's modulus of the obtained films were improved by the addition of nanolignin and could be used as competitive and green alternatives in the food packaging industry. In the literature, there are many studies on nanocellulose

and nanolignin, but no study has been found in which composite films are produced by using nanocellulose and nanolignin together. Makri et al. [31] created micro and nano scale preparations with 0.5% wt kraft lignin using the melt bonding method, reactive processing and in situ polymerization methods. It has been shown that polylactic acid (PLA) composites containing nanolignin produced via reactive processing have high crystallization, good mechanical and antioxidant properties, and reduction of lignin size has been successfully achieved with this reactive processing method. This situation has emerged as a result of the fact that the macro-scale reactive processing method of nanolignin is feasible, and it has been observed that nanolignin-grafted PLA composites improve its dispersion.

Zhang et al. [32], who included the use of pectin as a property modifier to improve the mechanical properties, hydrophobic properties, UV resistance and bioactivity of lignin-containing nanofilms, prepared composite films from pectin-based lignin nanoparticles especially for use in high-performance biobased food packaging. The physical, antioxidant and antibacterial properties of the composite films they prepared were systematically examined. The compatibility of lignin-containing nanoparticles within the pectin matrix and improvements in the mechanical and physical properties of the pectin-containing composite films were observed. As bioactivity behavior, they reported that pectin-containing lignin nanoparticle composite films significantly increased the antibacterial ability. As a result, they revealed that pectin–lignin nanoparticle composite films are especially suitable for use in food preservation and packaging applications. In another study by Yang et al. [33], nanoparticles were cross-linked by adding glutaraldehyde and citric acid to prepare PVA nanocomposites containing different lignin particles by weight with a simple solvent method. The optical, thermal, mechanical, antioxidant and antibacterial properties of PVA nanocomposite films were investigated in terms of their use as an active material in the food packaging industry. According to the results, it was emphasized that three different nanocomposites by weight, containing glutaraldehyde and citric acid, triggered strong interactions between lignin nanoparticles and PVA and showed significant antibacterial and antioxidant behavior.

In this study, the authors aimed to prepare cellulose/lignin nanocomposite materials with high thermal and mechanical properties. In this context, nanocomposite films containing lignin and cellulose in different ratios were prepared. The thermal properties of the films obtained were examined via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and their mechanical properties were examined via tensile test. In addition, the morphological structures of the samples were examined via SEM.

2. Materials and Methods

2.1. Preparation of Nanocellulose and Nanolignin

Nanocellulose was obtained according to the TEMPO method described by Peng et al. [34] Nanocellulose was obtained from 2,2,6,6-tetramethyl-1-piperidin-1-oxyl, which oxidizes alcohol groups in the cellulose chain in bleached softwood pulp to carboxylic acids.

Nanolignin was synthesized by modifying Frangville et al.'s methods [35]. Low-sulfonated lignin Indulin AT (MeadWestVaco Corporation, Richmond, VA, USA) was used as lignin starting material for nanolignin synthesis. 20 g of Indulin AT was dissolved in some distilled water, to which 1 M NaOH was added until the pH of the solution reached 11.44. A 7.7% Indulin AT solution was prepared by adjusting the final volume of the solution to 240 mL. The obtained solution was diluted and a 0.05% Indulin AT solution was prepared. HNO₃ was added to 10 mL of 0.05% Indulin AT solution until the pH was 1.97, and nanoparticles were obtained from the colloidal solution.

2.2. Preparation of Nanocomposite Films

The amounts of nanocellulose and nanolignin indicated in Table 1 were put into a beaker to prepare cellulose/lignin nanocomposite films. A 50 mL quantity of distilled water was added to the beaker. In order to obtain a homogeneous mixture, the obtained mixture was first kept in a magnetic stirrer and then in an ultrasonic bath at room temperature.

The resulting homogeneous mixture was poured into Petri dishes and dried in an oven at 40 °C for 48 h. Nanocomposite films were obtained by separating them from the Petri dish (Figure 1).

Table 1. Contents of cellulose/lignin nanocomposite films.

Sample	Nanocellulose (g)	Nanolignin (g)
F1	5	-
F2	5	0.125
F3	5	0.25
F4	5	0.5
F5	5	1

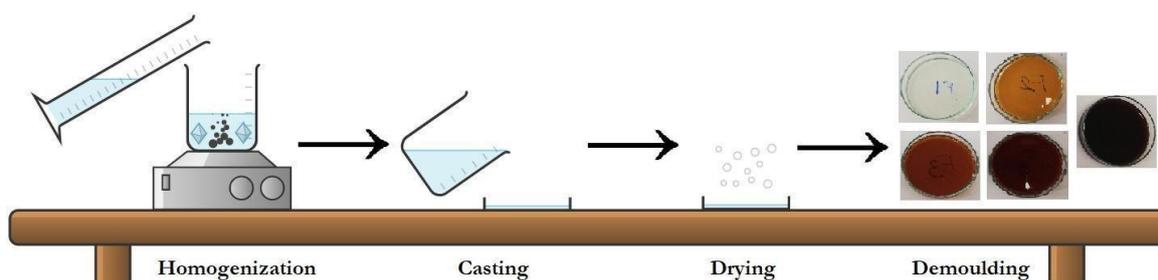


Figure 1. Schematic view of nanocomposite films.

2.3. Characterization

TGA was carried out under a nitrogen atmosphere at a heating rate of 10 °C/min between 30 and 750 °C using an Exstar TG/DTA 7200 model. DSC analyses were performed under a nitrogen atmosphere at a heating rate of 5 °C/min between 50 and 350 °C using a Perkin Elmer DSC 8000 model. The tensile test was carried out at a tensile speed of 100 mm/min until the samples broke. The test was repeated five times for each sample. SEM images were taken from the cut surfaces of the samples at different resolutions using a Tescan MAIA3 XMU model. Before analysis, samples were coated with platinum.

3. Results and Discussion

3.1. Thermal Properties of the Nanocomposite Films

TGA is an analysis method in which the mass losses of materials are examined under increasing temperature. In this thermal analysis method, a small amount of the sample is heated with a constant temperature rise. For this, a temperature increase of 10 °C/min is generally preferred. In samples showing large mass loss in a narrow temperature range, an increase of 5 °C/min is preferred. The mass loss data obtained from the temperature increase is plotted to obtain the thermogram of the material. In thermograms, the temperature increase on the *x*-axis and mass loss data in percent on the *y*-axis are processed to create graphs. In the resulting graphs, mass losses, usually in the range of 0 to 100 °C, are attributed to the output of water vapor or organic solvents. In the graphs, it can be seen that materials lose mass in one, two or three stages. The temperature at which the most mass loss occurs is considered the main decomposition temperature of the material. This temperature gives information about the maximum temperature at which the material can be used. The mass remaining at the final temperature at which the analysis is performed is the char yield of the material. Char yield gives information about the quantity of inorganic components remaining in the material depending on the atmosphere (air or nitrogen) in which the material is heated. By evaluating all these data obtained, interpretations are made about the thermal properties of the material.

TGA was used to determine the thermal stability of the obtained nanocomposite films. In this analysis, samples were heated from 30 to 750 °C at a heating rate of 10 °C/min. TGA and DTG thermograms of the nanocomposite films are shown in Figure 2. It was

determined that the samples underwent mass loss of 5% and 50%, reaching the maximum mass loss and residual ash yields at 750 °C. The data obtained from the thermograms are given in Table 2. As the nanolignin content increased, the initial decomposition temperature of the nanocomposite materials decreased from 77 °C to 60 °C. This is due to hydrogen bonds forming between -OH groups in cellulose and nanocellulose structures [36]. With the increase of nanolignin content, the main degradation temperatures of nanocomposite films clearly decreased. While the main decomposition temperature of the nanocomposite film without nanolignin was 334 °C, the main decomposition temperature of the sample containing 20% nanolignin was 288 °C. This decrease is due to the degradation of the structure of nanolignin at lower temperatures than the structure of nanocellulose. On the other hand, the char yield of nanocomposite films clearly increased with the increase of nanolignin content. While the char yield of the F2 sample containing 2.5% nanolignin was about 38%, the char yield of the F5 sample containing 20% nanolignin was about 42%. If the amount of nanolignin were increased too much, it was concluded that there would be no significant increase in char yield. Chollet et al. [37] prepared composite materials using PLA and micro- and nano-sized lignin. They reported that with increasing lignin content, the main degradation temperature of the composites decreased and the char yield increased.

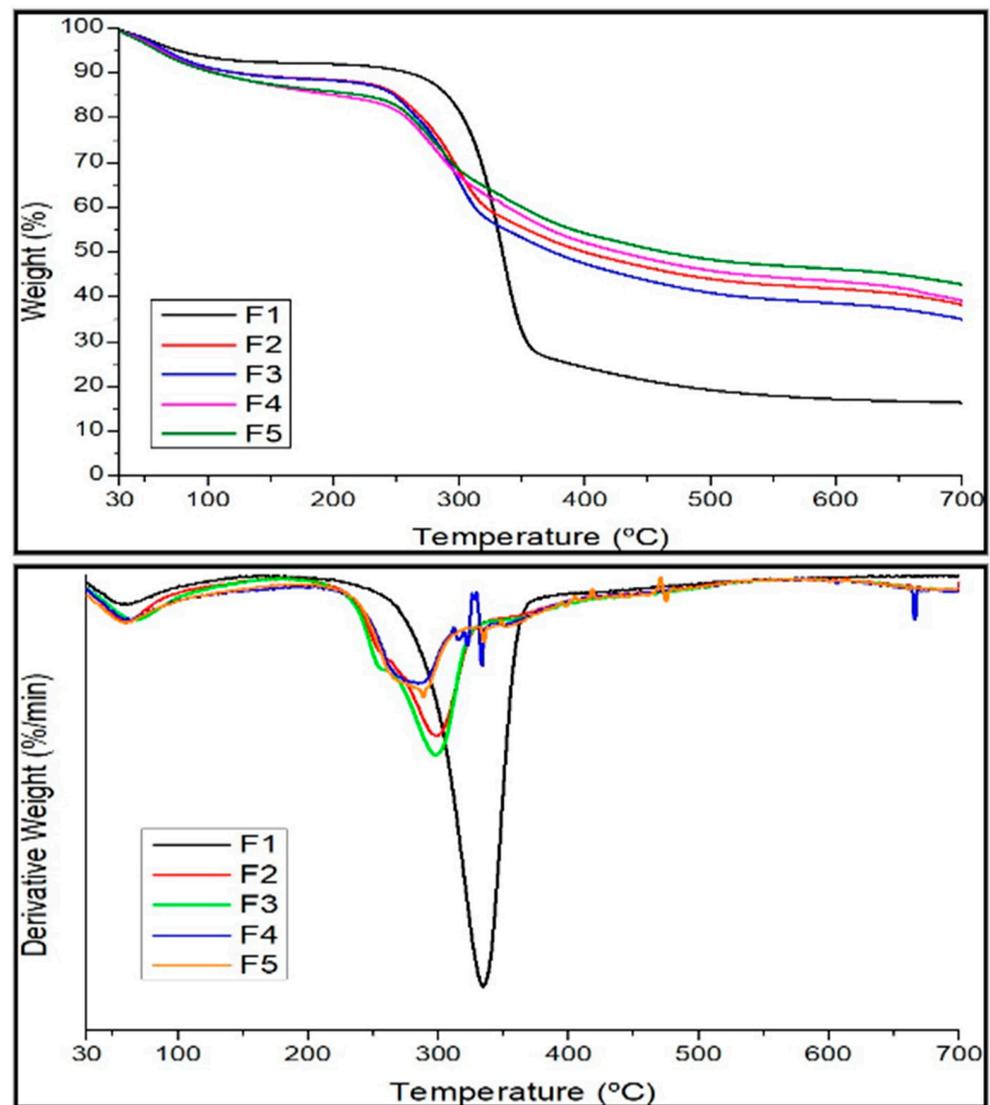
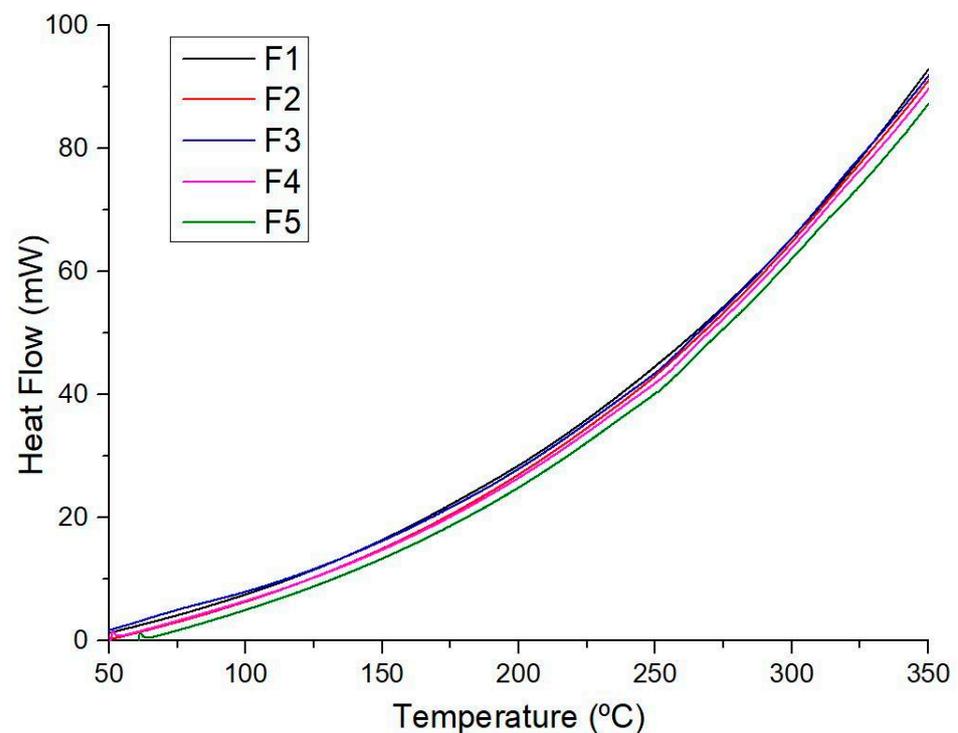


Figure 2. TGA and DTG of nanocomposite films.

Table 2. Thermal properties of nanocomposite films.

Sample	T5% (°C)	T50% (°C)	Max. Weight Loss (°C)	Char Yield (%)
F1	77	334	334	16.44
F2	62	400	298	38.13
F3	67	375	297	34.96
F4	63	428	287	39.05
F5	60	464	288	42.72

DSC was used to determine the thermal transitions of nanocomposite films. In the DSC technique, energy is needed to keep the sample and reference material at the same temperature while being heated or cooled. If there is a temperature difference between the sample and the reference material, the amount of energy supplied to the sample changes to keep the temperature the same. The change in the amount of heat during the phase change of the sample is detected. From the resulting curves, the glass transition temperature is determined from the shift of the baseline in the endothermic direction. The melting temperature of the sample is determined by the endothermic peak, and the crystallization temperature is determined by the exothermic peak. In addition, the enthalpy determination of the samples can be made. In this study, the samples were heated at a heating rate of 5 °C/min in the range of 50–350 °C. Figure 3 shows the DSC curves of the nanocomposite films. The results show that nanocomposite films do not have any thermal transition in the range of 50–350 °C. It is very difficult to detect thermal transitions of amorphous or densely cross-linked materials via DSC. The glass transition temperatures could not be determined because the obtained nanocomposite films are in amorphous structure and intense hydrogen bonds act as cross-links.

**Figure 3.** DSC curves of nanocomposite films.

3.2. Mechanical Properties of the Nanocomposite Films

The mechanical properties of the nanocomposite films were determined via tensile test. For this, a force was applied to the samples with a tensile speed of 100 mm/min until they broke. As a result of the analysis, the tensile strength and elongation at break of the samples were determined. The results obtained are shown in Table 3. With the addition of

2.5% nanolignin, the highest tensile strength was obtained as 13.38 MPa. With the increase of the amount of nanolignin, it was observed that the tensile strength values gradually decreased. One of the main factors affecting the mechanical properties of these materials is poor interfacial adhesion. One possible explanation is that it reduces the effect of stress transfer from the main matrix to the reinforcement component and reduces the strength of the composite. With the addition of nanolignin, an extreme decrease in elongation at break occurs and the material loses its flexibility and turns into a very hard and brittle form. From all these results, it can be said that the sample with the best mechanical properties was the F2 sample with the addition of 2.5% nanolignin. Makri et al. (2022) prepared bio-based PLA composites with nanolignin ratios in the range of 0.5% and 5%. It can be seen that the tensile strength increases with the addition of 2.5% nanolignin to PLA, and there is a decrease of more than 2.5% as in our study.

Table 3. Mechanical properties of the nanocomposite films.

Sample	Tensile Strength (MPa)	Elongation at Break (%)
F1	8.25 (± 2.62) ¹	15.58
F2	13.38 (± 0.37) ¹	2.62
F3	12.62 (± 0.95) ¹	1.88
F4	8.69 (± 1.98) ¹	1.59
F5	0.25 (± 0.31) ¹	Not observed

¹ Parenthesis indicate the standard deviation.

3.3. Morphological Properties of the Nanocomposite Films

With an increase of the reinforcing component used in nanocomposite materials, the irregularities in the morphology of the materials generally increase. For this reason, it is very important to examine the morphological structure when determining the correct amount of reinforcement. Morphological properties of nanocomposite materials were investigated via SEM. For this, the samples were cut, and the cut surfaces were coated with platinum before analysis. Figure 4 shows SEM images of composite films with different nanolignin filler ratios at different resolutions. It can be seen that as the amount of nanolignin increases, it decreases the resistance of internal adhesion with nanocellulose. The SEM images show where nanocellulose and nanolignin are compatible with each other and homogeneously dispersed within each other.

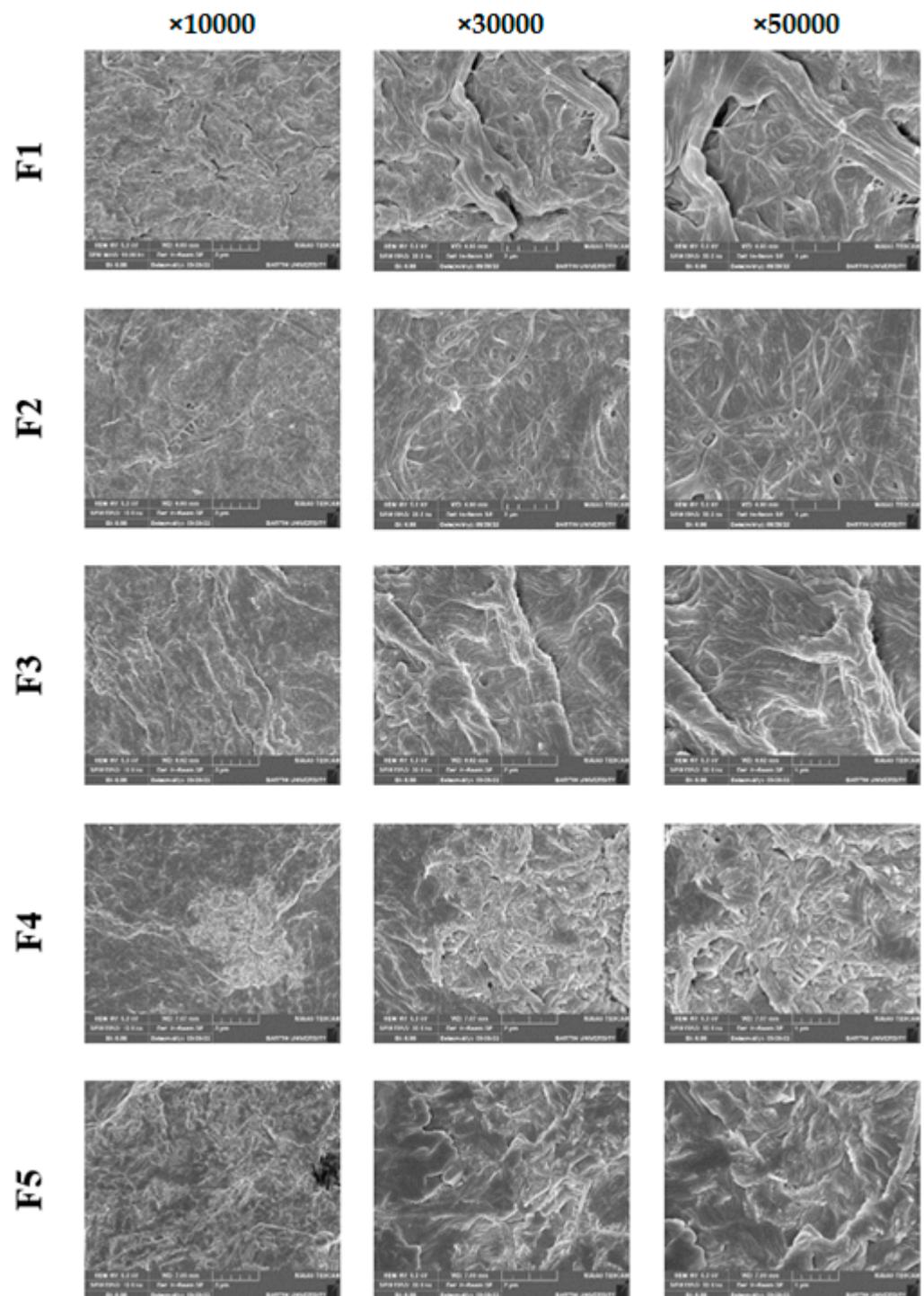


Figure 4. SEM images of the nanocomposite films.

4. Conclusions

In this study, it was the author's intent to prepare cellulose/lignin nanocomposite films and to examine their thermal, mechanical and morphological properties. Nanocomposite films containing different ratios of nanolignin were prepared. TGA results showed that initial mass loss and main decomposition temperature decreased with increasing nanolignin content, while char yield increased. Since the samples are amorphous and contain intense hydrogen bonds, the glass transition temperatures could not be determined via DSC. In the tensile strength test results, it was determined that the nanocomposite films had more structure with the increase of nanolignin content, and the sample with the

highest tensile strength was the F2 sample containing 2.5% nanolignin. From SEM images, it can be said that nanolignin and nanocellulose structure show homogeneous distribution and are compatible with each other. In this study, with the aim of obtaining a new, viable and environmentally friendly processing technology for producing lignin-containing cellulose nanomaterials, it has been shown that the newly developed lignin-containing cellulose nanofibrils achieve good thermal performance and surface properties compared to pure PVA. Increases in tensile stress and Young's modulus were observed. The films produced demonstrated the biodegradability of PVA composites to which lignin-containing cellulose nanofibrils were added, and their use in pharmaceutical carriers, packaging and various fields.

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