



Thermal Properties of Poly (Vinyl Alcohol) / Lignin Blends

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Abstract: In Libya, municipal and agricultural wastes are increasing each year leading to disposal problems. The use of municipal and agricultural wastes, particularly the natural polymers as compost are well known and the making of new products is receiving greater attention by researchers. The aim of this work was to study the thermal properties of biodegradable films which prepared from the reaction of PVA with lignin at a mass ratio of 1:2, 2:2, 3:2, and 4:2 respectively. Prepared biodegradable films used in this study have been thermally characterized by thermogravimetry (TGA) and differential scanning calorimetry (DSC) techniques. The results showed that the polymer blends were moderately thermally stable and the prepared PVA-lignin blended film may be potentially suitable as an eco-friendly packing material.

Keywords: Thermal; Properties; lignin; polyvinyl alcohol

INTRODUCTION

The use of biologically derived polymers (biopolymers) is emerging as an important component of economic development. By transforming forest and agricultural feedstocks, new renewable, biodegradable, and biocompatible materials (biomaterials) are being produced. Emerging applications for biopolymers range from packaging to industrial chemicals to medical implant devices and drug delivery to computer storage media. In addition to producing green materials with unique physical and functional properties, the processes used to create bio-based materials lead to new manufacturing opportunities that minimize energy consumption and waste generation (Mohanty, Misra, & Drzal, 2005). Owing to its biodegradability, renewability, abundance, and low cost, lignin is considered to be a good candidate as a functional filler and reinforcement for a variety of polymers. Several studies have shown that the use of lignin or lignin derivatives can improve the

mechanical and thermal properties of the polymeric materials (Kubo & Kadla, 2003; Xu, Ren, Wang, Sun, & Fang, 2013). Polyvinyl alcohol (PVA) is a nontoxic, highly polar, water-soluble, and biodegradable polymer which has been used in blends and composites with various polymers (Li, Lin, Zhuo, & Luo, 2013). PVA is widely used for packaging purposes, as an emulsifier, and as a sizing and coating in textile and paper industries (Chiellini, Corti, D'Antone, & Solaro, 2003).

A study conducted by (Tian et al., 2017) showed that the lignin nanoparticles were able to interact with the PVA macromolecular chains through hydrogen bonding and radical-scavenging reactions and also provide good interfacial adhesion between lignin and poly (vinyl alcohol). The use of lignin with PVA has been reported to form miscible blends and provide good thermal and mechanical performance, which has been attributed to the formation of strong intermolecular hydrogen bonds between the hydroxyl

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groups of PVA and lignin (Korbag & Mohamed Saleh, 2016; Tian et al., 2017). The objective of this study was to investigate the thermal properties of a lignin/PVA blend system using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

MATERIALS AND METHODS

The materials used in this paper are polyvinyl alcohol with molecular weight $M_w = 205,000$ purchased from Sigma-Aldrich, Germany, lignin, acetic acid, and distilled water.

Preparation of Films: Polyvinyl alcohol films were prepared using a casting method of aqueous polymer solutions. In order to improve the solubility of lignin, drops of acetic acid were added each half an hour and the solution was kept at pH 4 during the stirring and heating of the mixture at 80 °C for two hours. After that, various amounts of the PVA-lignin blends 1:2, 2:2, 3:2 and 4:2 were added respectively. The mechanical mixing was performed in a temperature range of 60–70 °C for 6 h. Finally, the mixture was poured into Petri dishes to make films. All films were kept for 1 h at 25 °C temperature and then oven dried at about 50 °C for 24 h. After drying, the films were peeled from the Petri dishes and stored in desiccators at room temperature.

TGA Analysis: The thermal degradation behaviors of polymer films and sample powders were studied using a Thermal Analyzer, Manufacturer and model: Mettler Toledo TGA/SDTA 851, fitted with Fourier Transform Infrared (Mettler Toledo). The samples of approximately 10 mg were placed into platinum pans and then heated from 50 to 900 °C at the heating flow rate of 10 °C. min^{-1} in nitrogen gas at the flow rate of 30 ml min^{-1} .

DSC Analysis: The compositional analysis and thermal stabilities of all polymer films and sample powders were studied and per-

formed on a Perkin-Elmer Pyris-1 Differential Scanning Calorimetry (DSC). The samples of approximately 5 mg were placed in aluminum pans and then heated from -50 to 150 °C at the heating flow rate of 10 °C. min^{-1} in nitrogen gas at the flow rate of 20 ml min^{-1} .

RESULTS AND DISCUSSION

TGA was used to investigate the thermal stability and degradation of pure PVA, lignin and PVA-lignin films. This analysis comprised various stages of moisture removal and weight loss as a result of heating. The PVA (black color curve in Fig.1) showed 8.60 % weight loss attributed to water removal in the first stage of heating which started at about 30 °C followed by thermal stability in the second stage. The most significant loss of about 47 % weight exhibits the decomposition of the side chain of PVA beginning at 209 °C. In the third stage, the weight loss of 29 % showed the decomposition of the main chain of PVA which was detected at 392 °C.

The last stage started at 498 °C, and the weight loss was 12 % which was attributed to the release of carbon dioxide. It can be clearly seen that the major weight losses were observed at about 76 wt % in the range of 200–450 °C which corresponded to the structural decomposition of PVA. This result was in agreement with (Othman, Azahari, & Ismail, 2011; Su et al., 2013). The initial thermal decomposition behavior of lignin (brown color) started at 29 °C with 13% weight loss due to water removal. The second stage of the decomposition appeared at 139 °C and showed a weight loss of 12 % due to the elimination of residue water. The third decomposition stage began at 295 °C with a weight loss of about 26 % which was attributed to volatile carbon dioxide. The last decomposition stage was started at 644 °C with 14 % weight loss due to volatilization of large amounts of carbon monoxide, and carbon dioxide generated by the breaking of the side chains.

This is in good agreement with results reported by (Hussin, Rahim, Ibrahim, & Brosse, 2013; Tejado, Pena, Labidi, Echeverria, & Mondragon, 2007).

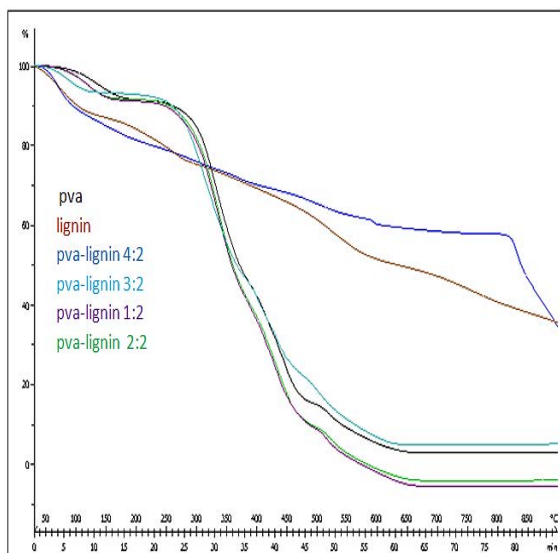


Figure: (1). TG-FTIR Thermogram of Pure Poly (vinyl alcohol), Lignin, and PVA-Lignin Films

Thermal decomposition behavior of four ratios 1:2, 2:2, 3:2 and 4:2 PVA-lignin blended films are shown in Fig. 1. The initial thermal decomposition behavior of 1:2 PVA-lignin film (dark blue color) started at 30 °C with 20 % weight loss due to water removal in the film. The second stage of decomposition appeared at 230 °C and showed a weight loss of 6 % due to the elimination of residual water. Third, fourth, and fifth decomposition stages showed an almost similar weight loss of 6 %, 5 %, and 7 % respectively, this is due to the decomposition of the main chains in the blended film. These stages were noticed at a range from 333.59 °C to 571.07 °C.

The last decomposition stage started at 785 °C with 23 % weight loss due to volatilization of large amounts of carbon monoxide and carbon dioxide generated by the breaking of the side chains in PVA-lignin film. This film has six stages which may be due to the amount of lignin added to the blended film is larger than the amount of polyvinyl alcohol.

TGA results showed that a PVA-lignin composite suppresses the thermal stability of PVA and there was intermolecular interaction between PVA and lignin as shown in Fig. 1. It is noted that, introducing lignin to the system decreases the thermal stability of PVA (Othman et al., 2011).

The initial thermal decomposition behavior of 2:2 PVA-lignin film (light blue color) started at 30 °C with 6 % weight loss due to water removal from the film. The second stage of decomposition appeared at 145 °C and showed the highest weight loss of 47 % exhibiting the decomposition of the main chains in PVA-lignin film. The third decomposition stage started at about 384 °C and showed a 10 % weight loss due to the decomposition of the side chain in the blended film. The fourth decomposition stage started at about 419 °C with 14 % weight loss due to volatilize gaseous generated the breaking of the side chains in PVA-lignin film. The final decomposition stage started at about 478 °C with 17 % weight loss due to volatilization of large amounts of carbon monoxide and carbon dioxide, which was generated by the breaking of the side chains in PVA-lignin film. This film has five stages, which may be due to the equal ratio of the blended film. The result in Fig. 1 showed that the thermal stability of the blends are slightly decreased due to the amount of lignin added to the amount of polyvinyl alcohol in the blended film, and also lignin was poorly dispersed in the PVA matrix. Therefore, the thermal stability of the blends was moderately thermally stable (Othman et al., 2011).

When the amount of polyvinyl alcohol is increased, the initial thermal decomposition behavior of 3:2 PVA-lignin films (violet color) started at 30 °C with 9 % weight loss due to water removal from the film. The second stage of decomposition observed at 196 °C and showed the highest weight loss of 51 % which exhibits the decomposition of the main chains in PVA-lignin film. The third decom-

position stage started at about 389 °C and showed a 30 % weight loss due to the decomposition of the side chain in the blended film. Fourth and last decomposition stage started at about 495 °C with 14 % weight loss due to volatilization of carbon monoxide and carbon dioxide which was generated by the breaking of the side chains in PVA-lignin film. This film has four stages which may be due to the high ratio of polyvinyl higher than the ratio of lignin in the blended film. It can be clearly noted that the major weight loss was observed at about 80 wt % in the range of 200-550°C corresponding to the structural decomposition of PVA - lignin.

The thermal stability of the reaction film has decreased due to the amount of polyvinyl alcohol added which was higher than the amount of lignin so the thermal stability of the film was lower than the stability of the PVA film. While when the amount of polyvinyl alcohol is increased, the initial thermal decomposition behavior of 4:2 PVA-lignin films (green color) started at 30 °C with 8 % weight loss due to water removal from the film. The second stage of decomposition was observed at 193 °C and showed the highest weight loss of 52 % which exhibits the decomposition of the main chains in PVA-lignin film. The third decomposition stage started at about 392 °C and showed a 29 % weight loss due to the decomposition of the side chain in the blended film. Fourth and last decomposition stage started at about 499 °C with a 13 % weight loss due to volatilization of carbon monoxide and carbon dioxide generated by the breaking of the side chains in PVA-lignin film. It can be clearly noted that the major weight loss was observed at about 80 wt % in the range of 200-550 °C which corresponded to the structural decomposition of PVA-lignin. The four blended films showed similar thermal decomposition behavior where all films showed a small mass loss in first decomposition stage and then more significant weight loss observed in second decomposition stage due to the decom-

position of the main chains in PVA-lignin film. TGA results showed that the thermal stability of the composite films was slightly improved when lignin was incorporated with PVA. These results were in agreement with a study reported by (Tian et al., 2017). The result showed that all blends are moderately thermally stable.

In Fig .(2) the PVA-lignin blended films and PVA film exhibited a fast weight loss in the vicinity of 285 °C and 350 °C respectively. The peak at around 285 °C of 2:2 blended films was short and broad. However, the other peaks around 350 °C of films had a similar behavior and they were long and sharp. The obtained results were in agreement with other works reported by (Su et al., 2013; Xu et al., 2013).

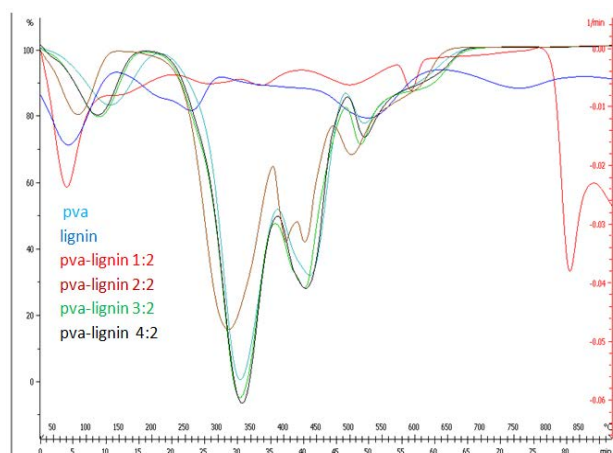


Figure (2). DTG Thermogram of Pure Poly (vinyl alcohol), lignin, and PVA-Lignin Films.

DSC is the technique used to determine the quantity of heat either absorbed or released when substances undergo physical or chemical changes. PVA is one of the partially crystalline polymers exhibiting both the glass transition temperature, T_g (characteristic of amorphous phase) and melting isotherm, T_m (characteristic of crystalline phase).

In Fig. (3), curve (a) shows the change of the thermal transition of pure PVA. The DSC curve of the Pure (PVA) showed one T_g ap-

peared at 52 °C while the sharp peak of crystallization temperature observed at 191 °C and ΔH of crystallization was 45 J/g while the DSC curve of lignin showed one Tg which appeared at 65 °C.

DSC curves of the four films showed nearly similar behavior. When the film ratio contains 1:2 PVA-lignin, the crystallization temperature decreased which observed at 186 °C, giving a small peak due to the blending of polyvinyl alcohol with lignin. The ΔH of crystallization is reduced to 21 J/g. While when the film ratio contains 2:2 PVA-lignin, the crystallization temperature decreased and observed at 188 °C given a broad peak due to the blending of polyvinyl alcohol with lignin. The ΔH of crystallization is reduced to 19.128 J/g.

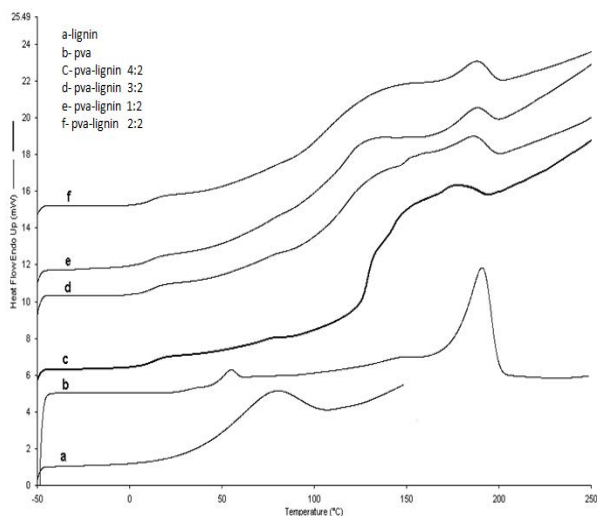


Figure (3). DSC thermogram of pure poly (vinyl alcohol), lignin, and PVA-Lignin films.

When the blend ratio contains 3:2 PVA-lignin, the crystallization temperature decreased and observed at 188 °C given a broad peak due to the blending of polyvinyl alcohol with lignin and the amount of polyvinyl alcohol is larger than the amount of lignin in the blended film. The ΔH of crystallization is reduced to 14 J/g. While when the film ratio contains 4:2 PVA-lignin, the crystallization temperature decreased and observed at 177

°C given a broad peak due to the blending of polyvinyl alcohol with lignin, and the amount of polyvinyl alcohol is larger than the amount of lignin in the blended film.

The ΔH of crystallization reduced to 10.19 J/g. It can be concluded that the higher the crystallization temperature (T_c) value, the more stable the molecules are, and that can be clearly seen in Fig. (3). PVA has more stable molecules than PVA-Lignin blended film. Fig. 3 showed that the crystallinity of PVA-lignin composites decreased slightly over the pure PVA due to the incorporation of the amorphous lignin. Disrupted hydrogen bonding network and new hydrogen bonds were formed between lignin and PVA matrix, leading to less crystalline regions formed in the composite films. Therefore, the blending with lignin reduced the crystallinity of the PVA fraction.

It is well known that in homogenized blends, the melting temperature shifts to the lower side. Melting enthalpy (ΔH_m) and crystallization enthalpy (ΔH_c) also showed a decreasing value with the incorporation of lignin, this indicates that there is an interaction between PVA and Lignin which has interrupted the crystallization of PVA. These behaviors showed the cumulative effects of PVA upon hydrolysis and also the reorganization in the degradation process. This finding has been supported by the results of other researchers (Jiang, Qiao, & Sun, 2006; Orts et al., 2007; Othman et al., 2011; Sarti & Scandola, 1995; Thakore, Desai, Sarawade, & Devi, 2001).

CONCLUSION

In this paper, the thermal behavior of PVA/lignin blends was studied. It appears that lignin is able to form hydrogen bonds with a semicrystalline and crystalline polymer, even though the blend system is slightly miscible. However, the blending with lignin reduced the crystallinity of the PVA fraction. TG and DSC analyses of polyvinyl alcohol

and lignin blends suggest that the blends were moderately thermally stable and also suggest intermolecular interactions between polyvinyl alcohol and lignin chains are favored. As a result, PVA/lignin blends may be useful for membrane and packaging applications.

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الخواص الحرارية لمزيج البولي فينيل الكحول واللجنين

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المستخلص: في ليبيا، تزداد النفايات البلدية والزراعية كل عام مما يؤدي إلى خلق مشاكل عند التخلص منها. إن استخدام النفايات البلدية والزراعية، وخاصة البوليمرات الطبيعية كسماد معروف جيداً، وعملية تصنيع منتجات جديدة تحظى باهتمام أكبر من جانب الباحثين. الهدف من هذا العمل هو دراسة الخواص الحرارية للأغشية القابلة للتحلل الحيوي والتي تم تحضيرها من تفاعل البولي فينيل الكحول مع اللجنين بمعدل كتلة 2:1، 2:2، 2:3، و2:4 على التوالي. الأفلام القابلة للتحلل البيولوجي المستخدمة في هذه الدراسة تم توصيفها حرارياً باستخدام تقنيات (TGA) و(DSC). النتائج بينت أن المزيج المكون من البولي فينيل الكحول واللجنين متوسط الاستقرار حرارياً وقد يكون مناسباً للاستخدام كمادة تعبئة صديقة للبيئة.

الكلمات المفتاحية: حراري؛ خواص؛ لجنين؛ بولي فينيل الكحول.