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THERMAL AND FTIR STUDY OF POLYVINYLPYRROLIDONE/LIGNIN BLENDS

M. F. Silva, C. A. da Silva, F. C. Fogo, E. A. G. Pineda and Anita A. W. Hechenleitner[*]

Departamento de Química, Universidade Estadual de Maringá, Av. Colombo 5790, 87020-900 Maringá, PR, Brazil

Sugar cane bagasse lignin (SCBL) was extracted with formic acid (FA) from a sugar and alcohol factory residue, and used for blends preparation with polyvinylpyrrolidone (PVP). Casting from DMSO and FA solutions were used as preparation procedure. PVP and PVP/SCBL blends were also irradiated with ultraviolet light (Hg lamp). Blend formation and irradiation effects were examined through thermogravimetric analysis (TG) and infrared spectroscopy (FTIR). Results suggest a greater interaction between PVP and SCBL chains in PVP/SCBL 95/5 cast from DMSO and in the 95/5 and 90/10 blends cast from FA. Pure PVP shows a thermal stability decrease due to irradiation and this effect is minimized in the PVP/SCBL blends. The initial stage of the thermal decomposition of PVP is anticipated by the SCBL incorporation.

Keywords: *blends, lignin, polyvinylpyrrolidone, ultraviolet irradiation*

Introduction

Lignin is the second most abundant natural polymer after cellulose, and is obtained mainly as a by-product in pulp and paper industry. Another important source of lignin is sugar cane bagasse, an agro-industrial residue obtained in great amounts in sugar and alcohol production industries. This amorphous, chemically complex polymer, is composed by phenylpropane units connected by various types of C–C and C–O–C linkages. In this way, a branched structure containing phenolic and aliphatic hydroxyles, methoxyls and carbonyls as principal functional groups results.

Several blends containing lignin or lignin derivatives as component or additive have been studied in recent years. The objective of those studies comprise various aspects such as to evaluate the intermolecular interactions, stability or miscibility of the polymeric materials [1–4], to examine applications for lignin that involve economically viable processes [5–9], among others. Other works have given emphasis to the possibility of improving some properties of materials by the lignin addition [10–12] based on its ability to act as antioxidant, stabilizer and filler. In spite of the dedicated efforts, the results have not attained the desired success. Among the reasons, there are the heterogeneity of this polymer, its complex chemical structure and the chemical modifications introduced by the processing conditions.

Blends preparation continues to be an attractive way to obtain polymeric materials with a variety of properties, through relatively simple and low cost procedures. Most of the physical properties of these materials depend, in one hand, on the chemical structure of the parent polymers and, on the other hand, on the preparation method. Both aspects are related to the nature and frequency of the intermolecular interactions developed between the polymeric chains.

Polyvinylpyrrolidone (PVP) is strongly adsorbed by unbleached kraft pulp and weakly adsorbed by bleached kraft pulp. It has been suggested that the PVP segments interact with the lignin of unbleached kraft pulp and mechanical pulps by hydrogen bond formation with catechol and phenol [13]. PVP has been used to stabilize cellulosic materials for electrical insulation and as a preservative polymer component to increase the dimensional stability of wood [14]. Furthermore, PVP has been investigated in blends with some hydroxyl-containing polymers such as poly(vinyl alcohol) [15], cellulose [16, 17] and polymethacrylates [18] where hydroxyl-bonding appears to be a major factor in inducing miscibility.

In this work, lignin (SCBL) was extracted from sugar cane bagasse for PVP/SCBL blends preparation. They were cast from dimethyl sulfoxide (DMSO) and from formic acid (FA) solutions and analyzed by thermogravimetric analysis (TG) and infrared spectroscopy (FTIR).

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[*] Author for correspondence: anitawh@uem.br

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Experimental

Materials

PVP of *Mw* 1300000 were purchased from Aldrich. Sugar cane bagasse was obtained from a local sugar and alcohol production industry (Santa Terezinha, Iguatemi). Hexane, FA, DMSO and other reagents used were of analytical grade.

Methods

For lignin isolation, sugar cane bagasse was first washed with abundant water, dried and grounded. This powder was submitted to successive extractions with *n*-hexane, ethanol and water in soxhlet system, to remove low molecular mass components. The sample was then treated with 80% FA and 1% HCl aqueous solution under reflux, for lignin extraction. The lignin was precipitated, diluting the dark brown solution obtained in the previous stage, in distilled water. Finally, lignin was isolated by centrifugation, washed with water, twice redissolved in FA for further purification, and oven dried at 60°C.

For blends preparation, the polymers (PVP and SCBL) were separately dissolved in DMSO and in FA, then mixed in appropriated amounts to give PVP/SCBL blends of 85/15, 90/10 and 95/5 mass/mass% ratios. The blend solution was stirred and then transferred to PTFE dishes for solvent evaporation at 60ºC.

PVP and PVP/SCBL samples were irradiated during 96 h with a Hg vapor lamp with 48 mJ s^{-1} m^{-2} of fluence rate.

FTIR spectra were performed on a FTIR Bomem MB 100 spectrometer and the samples prepared in 1% KBr pellets.

Thermogravimetric measurements were performed with a Shimadzu TGA 50 instrument in the following experimental conditions: approximately 6 mg samples, platinum pans, 10ºC min^{-1} of heating rate, 20 mL min^{-1} of nitrogen flux.

Results and discussion

PVP/SCBL blends were analyzed by their FTIR spectra. In compatible blends, chemical interactions or conformational changes are expected to cause spectral differences, which are often related to the carbonyl stretching vibration peak. In this case, the PVP carbonyl peak appeared at 1666 cm^{-1} shifted to lower frequency, due to lignin incorporation. The solvent used in the blend preparation seems to influence this behavior as it can be seen in Table 1, where a significant shift is observed in the blends 95/5 prepared in DMSO and 95/5 and 90/10 prepared in FA. The most probable interaction involving the PVP carbonyls is upon hydrogen bonding with the lignin hydroxyls, which can weaken the carbonyl bond and consequently its stretching vibration frequency should shift to lower values. Due to the branched structure of lignin it is also understandable that at low lignin content such interactions are favored because the inter-penetration between the chains is more likely to occur.

Table 1 Carbonyl peak frequency (±4 cm^{-1}) of the PVP, in PVP/SCBL blends, prepared by casting from DMSO and FA solutions

PVP/LBC	DMSO ν_{CO}/cm^{-1}	FA ν_{CO}/cm^{-1}
95/5	1652	1653
90/10	1662	1650
85/15	1663	1658

TG/DTG investigation of the samples were performed to study their thermal decomposition behavior. Figures 1 and 2 show curves of the pure polymers. The thermal decomposition of PVP starts at near 250°C and a sharp mass loss resulting about 70% change of the initial sample mass occurs between 370 and 430°C, where a well defined DTG peak centered at 420°C is observed. Another degradation stage is visible between 900 and 1000°C and about 2% of residual mass is present at this final temperature. SCBL initiates its thermal decomposition at 180°C which continues in several, not well defined steps, and a 25% of char yield is observed at 1000°C. Only one better defined DTG peak centered at 375°C is observed.

TG curves of PVP/SCBL blends showed mainly the PVP curve profile with little variations. In order to compare these results, two parameters (T_{max} and $T_{5\%}$) that can be used as a measure of thermal stability [12, 19–21], were computed. T_{max} is the temperature at which the degradation reaction attains a maximum

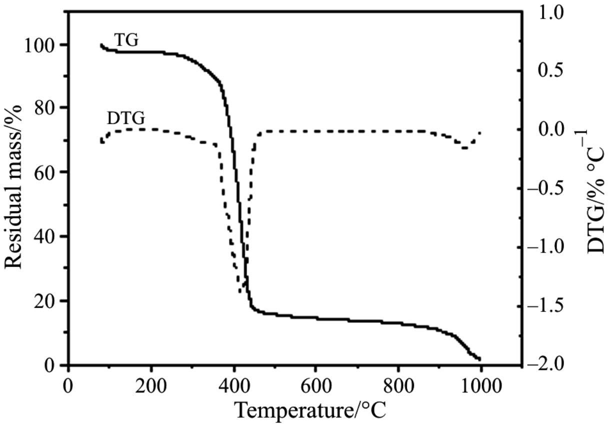

Fig. 1 TG and DTG curves of PVP

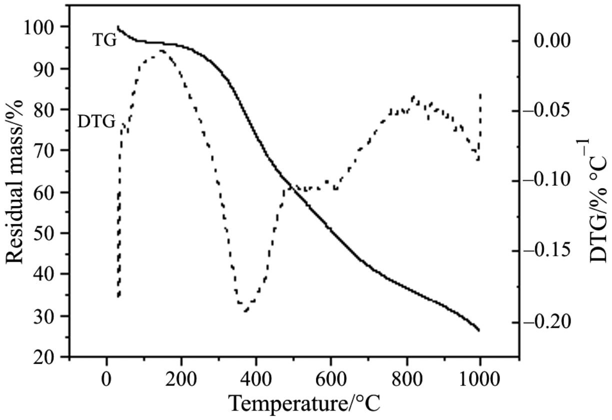

Fig. 2 TG and DTG curves of SCBL

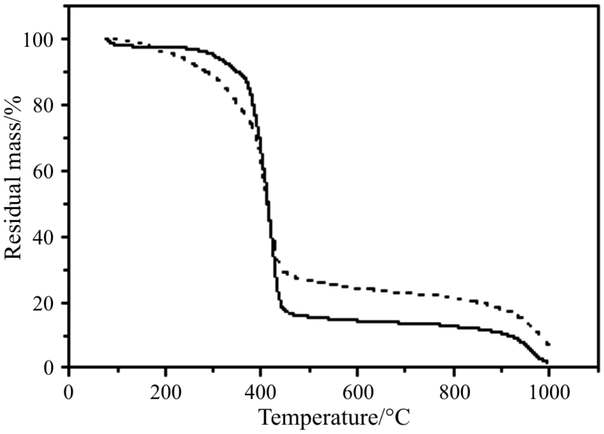

Fig. 3 TG curve of PVP,
— – before and --- – after UV irradiation

rate and corresponds to the minimum of the DTG peak. $T_{5\%}$ is the temperature at which the sample has lost the first 5% of mass after the water evaporation step (below 100°C). These data are listed in Table 2. T_{max}, which is 420°C for pure PVP, is practically not altered by the SCBL addition indicating that the principal thermal decomposition reaction of PVP is not influenced by the SCBL presence. On the other hand, $T_{5\%}$ (335°C for pure PVP) decreases by 9–40°C in the blends, showing that the PVP/SCBL system has lower initial thermal decomposition temperature than PVP.

Photostability of PVP and PVP/SCBL blends was also evaluated by TG. The samples were exposed to ultraviolet radiation of a Hg lamp, for 96 h and the analyses were performed before and after the irradiation. Changes in thermal behavior of PVP due to the irradiation are visible in the TG curve (Fig. 3). An acceleration of the initial stage of the thermal decomposition (160–380°C) and an increase in the residual mass between 430 and 1000°C take place. In the PVP/SCBL blends the effect in the initial stage of the thermal decomposition is minimized and it was quantified by the T_{max} and $T_{5\%}$ parameters (Table 3). The T_{max} of the pure PVP reduces from 420 to 412°C due to irradiation and the SCBL incorporation shows little effect also in the irradiated samples. The $T_{5\%}$ results show greater fluctuations, being 243°C for the irradiated PVP it amounts a difference of 92°C when it was compared to the not irradiated PVP ($T_{5\%}$=335°C). Comparing this PVP value with those of the irradiated PVP/SCBL samples, the differences in $T_{5\%}$ are smaller, except in the 95/5 blend prepared in FA. Thus, it can be said that SCBL has a certain ability to photostabilise PVP.

Table 2 T_{max} and $T_{5\%}$ data (see parameters definition in the text) for PVP/SCBL blends prepared by casting from DMSO and from FA solutions

PVP/SCBL mass/mass%	DMSO		FA	
	T_{max}/°C	$T_{5\%}$/°C	T_{max}/°C	$T_{5\%}$/°C
95/5	424	317	418	303
90/10	422	310	416	303
85/15	417	292	420	326

Table 3 T_{max} and $T_{5\%}$ data for PVP/SCBL blends prepared by casting from DMSO and from FA solutions, after irradiation with ultraviolet light for 96 h

PVP/SCBL mass/mass%	DMSO		FA	
	T_{max}/°C	$T_{5\%}$/°C	T_{max}/°C	$T_{5\%}$/°C
95/5	409	265	409	234
90/10	411	275	416	287
85/15	416	278	412	282

Conclusions

FTIR data suggest a greater degree of interaction between PVP and SCBL chains in blends with low SCBL content (5–10%), which depends on the solvent used in the preparation. Presence of SCBL (up to 15%) in PVP, in one hand, decreases its thermal stability but, on the other hand, increases its photostability.

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