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STUDIES ON THE THERMAL STABILITY AND FILM IRRADIATION EFFECT OF POLY(VINYLALCOHOL)/KRAFT LIGNIN BLENDS

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Lignin and poly(vinylalcohol) (PVA) solutions were separately prepared and then mixed in appropriate ratios, to yield the films after solvent (DMSO) evaporation. Two lignin samples were used: kraft lignin (KL) and acetone soluble fraction of kraft lignin (AKL). Different carbonyl and hydroxyl contents were detected by ^{1}HNMR and by FTIR for KL and AKL. PVA films containing up to 25% of lignin were prepared and irradiated with UV light for different time intervals. These films were analyzed using FTIR, TG and DSC. Due to the lignin incorporation in PVA films an increase in the thermal stability was observed. From DSC experiments, PVA/KL seems to provide a more homogeneous material compared to PVA/AKL, especially at 95/5 composition. PVA/KL films seem to have greater resistance to photochemical attack, as evaluated by crystallinity changes after irradiation of the film.

Keywords: *blends, lignin, poly(vinyl alcohol), ultraviolet irradiation*

Introduction

Lignin is an amorphous natural polymer constituted by a branched network of phenylpropane units. It acts as cementing agent between the cell walls of woody tissues and is a by-product of the pulping process in the paper industry. Because of its ability to act as antioxidant, filler, dispersant, binder, emulsifier and sequestrant, lignin has been investigated in several aspects [1, 2]. However, as definite utilization in large scale just the combustion for energy production has great industrial importance. Some properties can be improved by adding lignin or lignin derivatives to the polymeric materials [3, 4], but heterogeneity in its molecular size, bond energies and functional group distribution are indicated as complicating factors.

The presence of an antioxidant additive in plastics is essential especially if the polymer contains secondary or tertiary hydrogens and its final use include exposure to UV or ionizing radiation, heat or mechanical shear. Typical antioxidants are hindered phenols and secondary aromatic amines [5], which react with radicals forming resonance-stabilized radicals. Because of its phenolic structure, lignin is an excellent light absorber (190–400 nm, with peaks near 200, 230 and 280 nm), in which phenoxy radicals are the major intermediates formed when the samples were photo-irradiated [3, 6].

Two lignin samples (one being the acetone soluble fraction of the other) were selected for PVA/lignin blends preparation in this work. PVA films containing 5–25% of lignin were exposed to UV radiation and analyzed through FTIR and thermal analysis.

Experimental

Reagents and chemicals

Poly(vinylalcohol) 98–99% hydrolyzed, *Mw* 13000–23000, Lot N° 00221MZ, was purchased from Aldrich. Lignin was isolated from black liquor of kraft pulping process (Klabin from Paraná State, Brazil). The purity of all other reagents were not less than 99%.

Methods

Concentrated black liquor was obtained from a paper and cellulose production industry (Klabin from Paraná State, Brazil). An aliquot amount of this liquor was diluted with water, hot filtered for fibrous material separation, acidified with sulfuric acid to reach pH=11 and the colloid sulphur was separated by centrifugation. Lignin was then precipitated at pH=3 (hydrochloric acid solution was added) and separated by centrifugation. This lignin sample (KL) was twice dissolved in alkaline aqueous solution, precipitated in acid aqueous solution and isolated by centrifugation. Finally, dried in an oven at 60°C.

Fractionation of lignin was carried out in soxhlet apparatus, firstly the ethyl ether soluble fraction (about 1% in mass) was removed from the original kraft lignin. From the sample obtained in this way, the acetone soluble fraction (AKL) was then isolated.

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This fraction, corresponds to near 50% in mass of the starting lignin sample.

For blends preparation, lignin and PVA were dissolved separately in DMSO. Appropriate volumes of these solutions were mixed and stirred at room temperature. PVA/lignin solutions (100/0, 95/5, 85/15 and 75/25) were then poured in PTFE molds and placed in a vacuum oven (60°C, 0.5 atm) until total solvent evaporation.

Films were irradiated with a Hg vapor lamp with 48 mJ s^{-1} m^{-2} of fluence rate.

KL and AKL were twice acetylated by treatment with acetic anhydride–pyridine (1:1) for 24 h treatment, followed by purification and drying [7]. ^{1}HNMR spectra of acetylated KL and AKL were recorded on RMN-Gemini-300 BB spectrometer. $CDCl_3$ was used as solvent and TMS as internal reference. Other conditions used were: magnetic field of 300 MHz, acquisition time of 2.5 s, 128 scans, room temperature.

The IR spectra of the samples were recorded on a FTIR Bomen MB–100 spectrophotometer in KBr pellets or films.

Differential scanning calorimetry (DSC) was performed using a Shimadzu DSC-50 instrument at a heating rate of 10 K min^{-1}, in a N_2 atmosphere at a flow rate of 20 mL min^{-1}. Samples of about 6 mg were used, they were preheated to 130°C for water evaporation. The instrument was calibrated with indium and zinc standards. The distortion of the PVA melting peak, namely its broadening at the left of the peak, due to lignin addition and/or film irradiation, according to the a:b ratio (Fig. 1) was determined.

Thermogravimetric analysis (TG) was carried out on a Shimadzu TGA-50 analyzer, at a heating rate of 10 K min^{-1} in flowing N_2 (10 mL min^{-1}). Sample mass was also about 6 mg, they were maintained in silica gel containing desiccator.

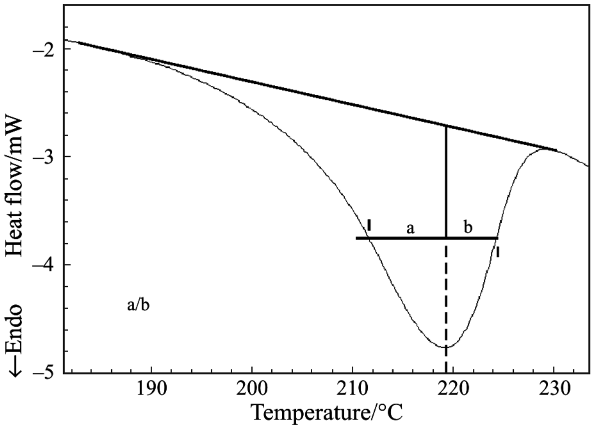

Fig. 1 DSC curve of a PVA/lignin blend showing the baseline and the definition of a and b distances

Results and discussion

KL and AKL were comparatively investigated in relation to functional groups content through FTIR and ^{1}HNMR spectroscopy. From FTIR spectra, the maximum absorbance of the hydroxyl characteristic band (near 3400 cm^{-1}) and of the carbonyl characteristic band (about 1715 cm^{-1}) were each divided by the absorbance recorded at 1500 cm^{-1}, which is characteristic for the CH vibration of the aromatic ring (internal reference). Based on this data (Table 1), KL has a higher hydroxyl and lower carbonyl content than AKL. From the ^{1}HNMR spectrum of acetylated KL and AKL, the peak area at 2.0 ppm (protons of aliphatic acetate, originated from the aliphatic hydroxyles) and the peak at 2.3 ppm (protons of aromatic acetate, or phenolic hydroxyles in the underivatized lignin) were computed and divided by the sum of the area of all peaks present in the corresponding spectrum. These results reveal a greater phenolic hydroxyl content in KL as it has been compared to AKL (Table 1).

Table 1 Peak absorbance (Ab) ratios calculated from infrared spectrum and peak area (Ar) ratios from ^{1}HNMR spectrum, of KL and AKL lignin samples

	KL	AKL
Ab_{3400}/Ab_{1500}	0.85	0.67
Ab_{1715}/Ab_{1500}	0.40	0.69
$Ar_{2.0}/Ar_{total}$	21.20	21.50
$Ar_{2.3}/Ar_{total}$	17.00	11.50

Films were prepared with pure PVA and with PVA/KL and PVA/AKL blends. FTIR, DSC and TG traces from these samples were recorded. The TG results obtained with the PVA and PVA/KL systems are shown in Fig. 2. The main degradation step (where the greater degree of mass loss occurs) in PVA, between 250 and 300°C, is shifted to higher temperature in the presence of KL. Therefore, a thermal stability gain due to lignin incorporation in PVA films is evidenced. The effect increases with increasing lignin content, and PVA/AKL blends show similar results. TG curves of KL and AKL are shown in Fig. 3, both show lower initial temperature of degradation (after water elimination) than PVA. KL and AKL differ in the initial temperature of degradation which is 170°C for KL and 140°C for AKL. AKL also degrades more rapidly up to 250°C and at higher temperatures the TG curve profile of both samples are very similar. At 1000°C the residual mass is 42% for KL and 38% for AKL. In order to quantify the mentioned thermal stability increase of PVA due to lignin incorporation, a TG curve was constructed for the PVA/KL 85/15 blend by the linear combination of the pure polymer curves in the desired proportion. When these curves coincide, it is considered that in the blend the polymers are present as independent phases. The results obtained are shown in Fig. 4, where in the 87 to 30% of residual mass interval, the experimental curve shows about 45°C shift towards higher temperatures when compared to the calculated curve. Consequently, a significant interaction at molecular level is expected between PVA and lignin macromolecules.

Glass transition temperature (T_g) data are not informative because it was not possible to detect the T_g of lignin undoubtedly from the DSC curves. The melting of PVA takes place between 200 and 235°C and the thermal decomposition starts near 220°C.

The PVA, PVA/KL and PVA/AKL films were irradiated with UV light and also analyzed through FTIR and DSC. It was observed that the melting peak of PVA are broadening in the DSC curves when lignin is incorporated and when the films are irradiated. The effect was measured through the a/b parameter, calculated as detailed in the 'Experimental', and the results are listed in Table 2. The dislocation of the peak towards the lower temperature region indicates that a solution of the two components took place, where the presence of the solute (lignin) causes a melting point depression for the solvent (PVA) [8]. Therefore, higher a/b values are most probably indicating that a greater degree of mixing at molecular level between the chains of the components is attained, which is the case of the PVA/KL 95/5 system. The a/b ratio was tended to decrease after film irradiation, that can be related to some phase separation and/or PVA chain scissions, providing a greater fraction of PVA with lower molar mass in crystalline regions, which melts at lower temperature.

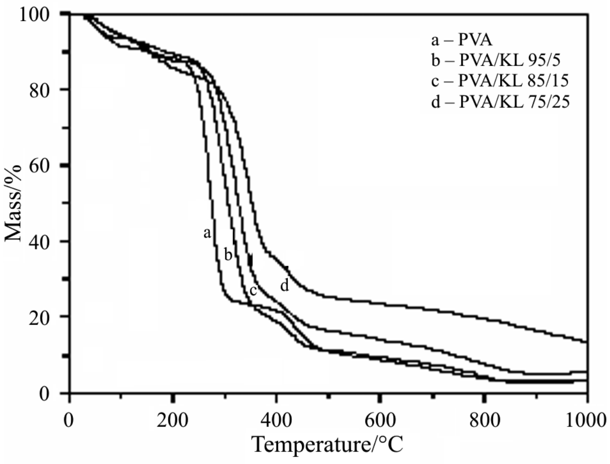

Fig. 2 Influence of the kraft lignin incorporation in poly(vinylalcohol) films on the TG curve

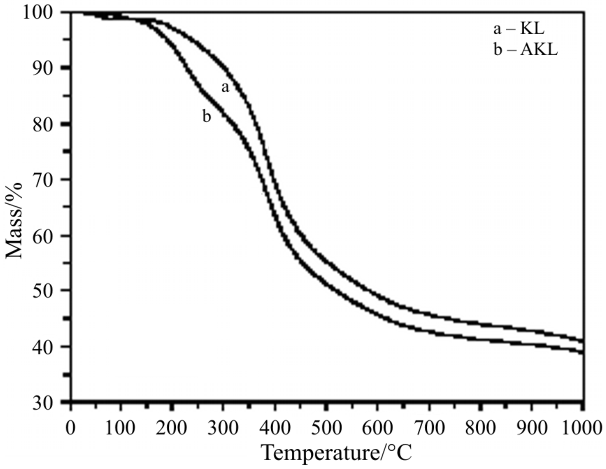

Fig. 3 TG curve of kraft lignin and of its acetone soluble fraction

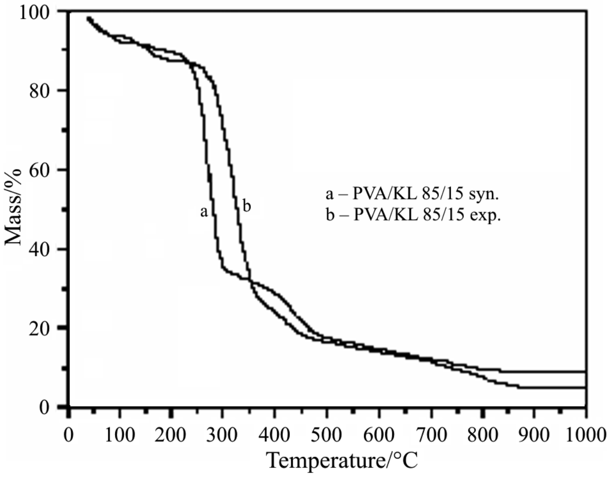

Fig. 4 Comparison between a – synthesized and b – experimentally recorded TG curve of the PVA/KL 85/15 blend

In order to evaluate crystallinity changes in PVA due to lignin incorporation and to film irradiation, a relative crystallinity index was determined from the FTIR spectra. This parameter is calculated as the absorbance at 1143 cm^{-1} (PVA crystalline absorption band) divided by the absorbance at 2908 cm^{-1} (PVA internal reference band). The determination of the maximum absorbance of the methylene stretching band (at 2908 cm^{-1}) included the deconvolution of the bands between 2800

Table 2 PVA melting peak broadening (a/b) in PVA films at different compositions, before and after irradiation with UV light

Film composition	Not irradiated	Irradiated for 96 h
PVA	2.0	2.1
PVA/KL 95/5	2.8	2.5
PVA/KL 85/15	2.5	2.5
PVA/KL 75/25	2.6	2.3
PVA/AKL 95/5	2.3	2.1
PVA/AKL 85/15	2.4	2.2
PVA/AKL 75/25	2.5	2.2

Table 3 PVA crystallinity index calculated from FTIR spectra (Ab_{1143}/Ab_{2908}), in PVA films with different compositions, before and after irradiation with UV light

Film composition	Non-irradiated	Irradiated for 96 h
PVA	0.98	1.05
PVA/KL 95/5	1.07	1.02
PVA/KL 85/15	1.11	1.11
PVA/KL 75/25	1.18	1.22
PVA/AKL 95/5	0.95	1.04
PVA/AKL 85/15	1.03	1.11
PVA/AKL 75/25	1.04	1.15

and 3000 cm^{-1} into individual peaks, obtaining three for PVA, six for KL and seven for AKL. This band deconvolution is also necessary in the lignins spectra to elucidate if the additivity of the absorbance is preserved in that region, in the spectra of PVA/lignins. The applied procedure is described in [9]. The obtained results are reported in Table 3 where small variations in the crystallinity index are observed. Due to irradiation a significant increase only in the case of pure PVA and in the PVA/AKL films could be observed. Such increase in the crystallinity appears most probably because of the decrease of the amorphous fraction, i.e. some amorphous PVA should be destroyed during irradiation. In this way, KL seems to provide a better protective effect when photoinduced reactions occur preferentially in the lignin chains, and leaving the PVA chains unaltered. This fact is supported by the higher phenolic hydroxyl content in KL group which is responsible for the antioxidant character of lignin, through stable phenoxy radicals formation.

Conclusions

It was possible to prepare PVA films containing up to 25% of two lignin samples, denoted as KL and AKL. AKL is the acetone soluble fraction of KL. FTIR and ^{1}HNMR spectra showed that KL contains more phenolic hydroxyl and less carbonyl groups, than AKL. An increase in the thermal stability due to lignin incorporation in PVA films was observed comparing the TG curves obtained experimentally to the simulated TG curve. As it has been concluded from the DSC analysis, PVA/KL blends seem to provide a more homogeneous material, mainly at 95/5 composition. KL also shows a better photo-protective effect for the PVA polymer, because PVA/KL films do not change their crystallinity upon irradiation. PVA and PVA/AKL films show crystallinity increase due to irradiation which can be related to amorphous PVA destruction during irradiation.

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