THERMAL STABILITY AND MISCIBILITY OF CELLULOSE ACETATE AND INDUSTRIAL WASTE LIGNIN BLENDS

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Abstract

The thermal properties and miscibility of cellulose acetate (CA) and industrial waste lignin (L) blends were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and Fourier transform infra-red spectroscopy (FTIR) over the entire range of composition. The lignin was blended up to 50 wt% with cellulose acetate. The blends were prepared by solution blending method. Although the lignin shifts the onset of CA decomposition to lower temperatures, the CA/L blends are thermally more stable than CA over the wider temperature range. The TGA results suggest all blends are compatible. These results correlate well with the glass transition temperature (T_g) data where single T_g obtained for all these blends. There is a slight decrease in T_g as the lignin wt% increase in blends, where in (70/30) composition it shows higher value than CA. There is no phase separation was found in SEM images of blends. The FTIR analysis revealed the formation of blending between CA and Lignin.

Keywords: Cellulose acetate, Lignin, Thermal stability, DSC, SEM, FTIR.

1. Introduction

Blending of polymers is one of the simplest means to obtain a variety of physical and chemical properties from the constituent polymers. The gain in newer properties depends on the degree of compatibility or miscibility of polymers at molecular level.[1] The utilization of lignin biodegradable/ biobased material is receiving increasing attention as the world looks to find alternatives to petrochemicals. Traditionally, lignins have been incorporated into various polymeric materials as low cost filler.[2] Lignin exists in plant cell walls and second only to cellulose in overall natural abundance. Lignin is a complex, amorphous, polyphenolic, natural organic polymeric material and built up from poly

phenyl propane units. Enormous quantity of industrial lignin is produced as a byproduct of papermaking. Kraft/ alkaline and sulphite process are the two main delignification processes in pulping industry, thus lignin is removed from wood, due to the fact that lignin is available in large quantities from pulp mills.[3] Depending on the type and length of chemical processing, the lignins vary in molecular weight, functional groups present, degree of condensation, types of inter monomeric linkages and the type and ratio of monomeric units.[2]

Rials et al. prepared the blends of hydroxypropyl cellulose (HPC) and organosolve lignin (OSL) by mixing solutions of both pyridine and dioxane, and casting as a films, and by mixing in the melt by extrusion and studied its mechanical properties and SEM, DSC, WAXD and DMTA analysis.[4] Similarly, they prepared blends of lignin with ethyl cellulose (EC) and cellulose acetate/ butyrate (CAB) by solution casting from dioxane and studied dynamic mechanical analysis (DMTA) and DSC analysis.[5] Girdthep et al. studied the effect of Tween 80 on the mechanical and thermal properties of solution caste blends of poly (lactic acid) and cellulose acetate butyrate films.[6] Chen et al. prepared the microfiltration membrane by blending a matrix polymer with functional polymer. The effects of the time phase inversion induced by water vapor, blended amount of PEI and amount of crosslinking agent on membrane performance was investigated.[7] Literature survey reveals that various researchers[8-10] blended lignin with polymers like poly (vinyl alcohol), poly (ethylene oxide), poly (ethylene perphthalate), poly (propylene) and studied of their thermal properties, chemical structure and molecular interactions.

Cellulose acetate is a plastic produced by the action of acetic anhydride on cellulose in presence of either sulphuric acid or perchloric acid as a catalyst.[11] It can be used for various applications (eg. For films, membrane or fibers).[13] In the present study cellulose acetate has been blended with industrial waste lignin by solution blending.[11,12] The solid

state miscibility was studied by analyzing DSC and SEM of blends. The thermal degradation behaviors of the blends were studied by thermogravimetric analysis. The molecular interaction and bonding was investigated by FTIR.

2. Materials and methods

2.1   Cellulose acetate

CA was obtained from Lobachemie. Its Melting point is 240 °C, acetyl content is 29-45%, Mol. Wt. is 316.39, density is 1.3 g/ml at 25 °C, and refractive index is 1.475.

2.2   Lignin extraction

Lignin has been precipitate from black liquor procured from nearby paper industry using 20% sulphuric acid. The precipitate obtained was thoroughly washed with water and filter. The residue was dried and weighed. The crude lignin was purified using 1,4 dioxane.

2.3   Lignin characterization

2.3.1 Elemental analysis

Carbon, hydrogen and nitrogen contents were determined using Thermo Finnigan CHN Analyzer.

2.3.2 FTIR analysis

The FTIR spectra of lignin was obtained with a Happ-genzel spectrometer using resolution 4.0 cm^{-1} and 40 addition scans in a frequency range of 400-4600 cm^{-1}.

2.3.3 Ultraviolet spectroscopy

The absorbance of lignin solution in ethanol was recorded on different wavelengths within a range 200-400 nm to find out λ_{max} on UV spectrometer.

2.3.4 Thermal analysis

Thermal analysis is very useful in the determination of thermal stability and effective temperature range for thermal degradation of lignin.

Thermal investigations were carried out on Mettler Star SW 9.2 with heating rate 10 $^{\circ}$C per minute in inert atmosphere.

2.4 Blend preparation

The CA/L blends were prepared by mixing the individual solutions (wt %) of components in 1,4 dioxane. The components get dissolved in the solvent. The solutions were mixed together and stirred for approximately half an hour. The resulting solution mix was poured in small installments in large quantity of distilled water (non-solvent of CA and lignin). There is a formation of precipitate of blend in water, which was then immediately pick out from water with the help of glass rod and placed on filter paper. The blends then dried in air at room temperature for 4-5 days. The dried blend then crushed to fine powder with the help of mortar and pestle. It was then used for further analysis. The compositions of blends were obtained by mixing wt% solutions of CA and lignin as given in Table.1

Sr. no.	Blend composition (CA/L)	CA solution (wt %)	Lignin solution (wt %)
1.	90/10	9	1
2.	70/30	7	3
3.	50/50	5	5

Table.1. CA/L blend preparation

2.5 Characterization of blends

2.5.1 Thermogravimetric analysis (TGA)

The thermal decomposition studies were carried out in TA instrument Dimond TG/DTA (Perkin Elmer, USA). Heating was carried out at a rate of 10°C/min from 25°C to 820°C. The test was performed in an atmosphere of nitrogen.

2.5.2 Differential Scanning Calorimetry (DSC)

The DSC scans were collected in NETZSCH DSC 204 instrument heated from -25°C to 350°C at a heating rate 10°C/min in nitrogen atmosphere.

2.5.3 Scanning electron microscopy (SEM)

The morphology of CA/L blend was examined using scanning electron microscope, type JEOL Model JSM-6390LV at an accelerating voltage 20 kV with SEI image mode and 1µm resolution.

2.5.4 Fourier transform infra-red spectroscopy (FTIR)

IR spectra were collected using Nicolet MAGNA 550 (Nicolet Instrument Corporation, USA) in a spectral range 4000-400 cm^{-1} using 64 scans at 4 cm^{-1} resolution.

3. Results and discussion

3.1 Analysis of lignin

Elemental analysis of lignin gives 61.2% carbon content, 5.9% hydrogen content, 32.9% oxygen content and 0% nitrogen content.

The FTIR spectra show a broad band at 3404 cm^{-1} attributed to OH group, 2936 cm^{-1} predominately arising from CH stretching in aromatic methyl and methylene groups of side chains, 1718.8 cm^{-1} originating from unconjugated carboxyl/ carbonyls stretching with shoulder around 1655.6 cm^{-1}, aromatic skeletal vibrations are observed at 1516.2, 1458.4 and 1425.6 cm^{-1} is obtained. The CH deformation in CH$_3$ is found at 1363.8 cm^{-1}. The spectra show the various characteristic for syringyl unit at 1329 cm^{-1}, 1213.4 cm^{-1} for CO stretching and 1116.9 cm^{-1} CH in plane deformation. The guaicyl unit shows vibration at 1032 cm^{-1} for aromatic CH in plane deformation. [14-15]

The lignin solution in ethanol gives absorbance maxima at 234 nm. This maximum absorbance can be assigned to phenolate ion compound and guaicyl lignin structures analysed by ultraviolet spectroscopy.[16]

The TGA curve shows that lignin starts decomposition at 109.8 ˚C. At 372˚C the weight loss reached up to 51.48%. At 604˚C 68% lignin was degraded.

3.2 Analysis of blends

Thermal stability of CA and CA/L blends were assessed. The TGA thermogram for CA and CA/L blends are shown in Fig.1. Cellulose

acetate shows single stage degradation, the temperature at which it starts to decompose is at 300 ˚C and ends at 425 ˚C where the weight loss percentage is 87.6%. Similarly, all the CA/L blends of composition 90/10, 70/30 and 50/50 show single stage degradation at a temperature range 295-425 ˚C, 275-395˚C and 245-395 ˚C respectively. This indicates that the decomposition temperature decrease slightly in blends as compared to CA. The weight loss percentage of CA at 802˚C is 95.1%, where as CA/L blends of composition 90/10, 70/30 and 50/50 were 98.1%, 93.3% and 84.2% respectively. The decrease in wt. loss with increase in lignin content in blends is indications that blend are thermally more stable than CA in wider temperature range. Similar kind of results were obtained for poly (hydroxybutyrate) and soda lignin blends by Mousavioun et al.[17]
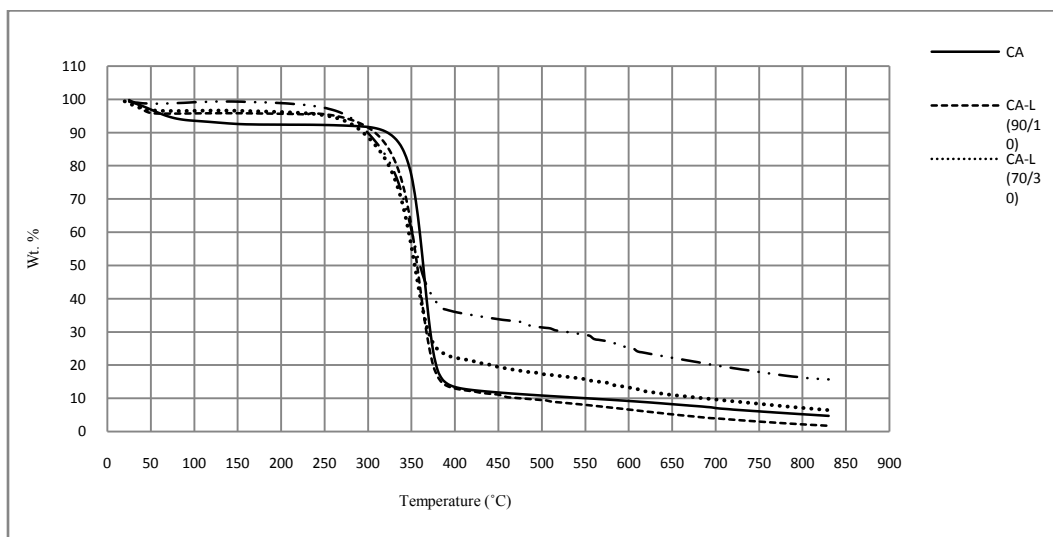

Fig.1 TGA curves of CA and CA/L blends

The most accepted parameter to assess polymer miscibility is the T_g. A single T_g of blend implies complete miscibility between the polymer pairs in their amorphous fractions. Fig.2 shows the DSC curves of lignin, CA and CA/L blends where the T_gs were obtained. The T_g was taken as midpoint of the change of slopes in DSC curves. Fig.2 illustrates the T_g of lignin at 59 ˚C. The T_g of CA was found to be at 52 ˚C, which shows correlation with the literature data.[18] The DSC curves in Fig.2 for CA/L

blends shows single T_g at 45 °C, 53 °C and 42 °C for 90/10, 70/30 and 50/50 compositions respectively. The single T_g is the indication that all blends are miscible. There is decrease in T_g in 90/10 and 50/50 blends but the T_g of 70/30 blend is 53 °C which is higher than T_g value of CA. This result is very much similar with those of Kubo et al.[2, 10]
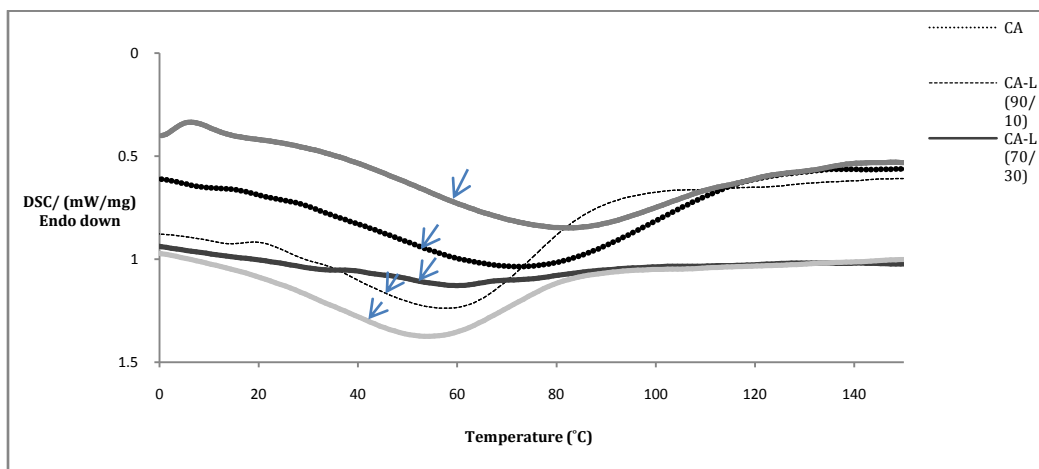

Fig.2 DSC curves of lignin, CA and CA/L blends

Scanning electron microscopy (SEM) is the powerful technique to determine miscibility of blends.[1] The lignin, CA, 90/10, 70/30 and 50/50 CA/L blend compositions was examined through SEM and corresponding micrographs are shown in Fig.3 (a, b, c, d and e). There was no apparent phase separation observed. Thus the SEM data follow similar trends as the data obtained from the T_g of blends.
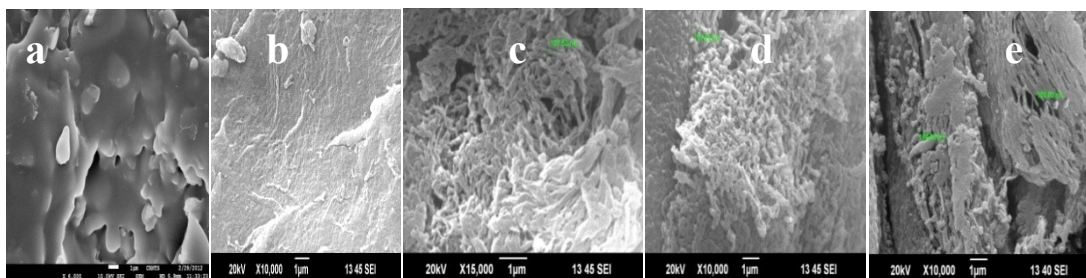

Fig.3 SEM image of a) lignin b) Cellulose acetate c) CA-L (90/10) d) CA-L (70/30) e) CA-L (50/50)

Attempts in understanding the miscibility of the lignin-polymer blends have been made using FTIR as have been undertaken by previous workers Kubo et al., Maldhure et al. and Fan et al.[19-21] Infrared spectroscopy have been proven to be a highly effective means of investigating specific interactions between polymers. Fig.4 shows the FTIR spectra from 3482 to 3488 cm^{-1} for O-H streching (intramolecular hydrogen bonded) for CA and CA/L blends. The blends and CA show C-H streching In methyl/ methylene group in region 2948- 2931 cm^{-1}. The CA curve shows a peak for O-H streching. in –COOH at 2635.41 cm^{-1}. The –C≡C- streching for alkynes was found in the 2129- 2123 cm^{-1} in CA and CA/L blends except 50/50 composition. There are peaks in curve of CA and blends for C=O (esters) in the range 1751-1749 cm^{-1} and C=C str. (alkenes) in 1639-1609 cm^{-1} region. The spectra shows strong peak at 1236 cm^{-1} and at 1046 cm^{-1} in all the curves which was attributed C-O streching (esters). The peaks at region 904- 902 cm^{-1} assigned to C-H aromatic deformation (monosubstituted). Peaks centered at 835- 833 cm^{-1} assigned to C-H aromatic deformation (disubstituted) were found in curves of 70/30 and 50/50 blend composition. The region from 606- 604 cm^{-1} attributed to ≡C-H bending alkynes (RC≡CH) was found in all the curves of blends and CA. These results indicate that, the reactive functional groups of lignin form bonding with CA.
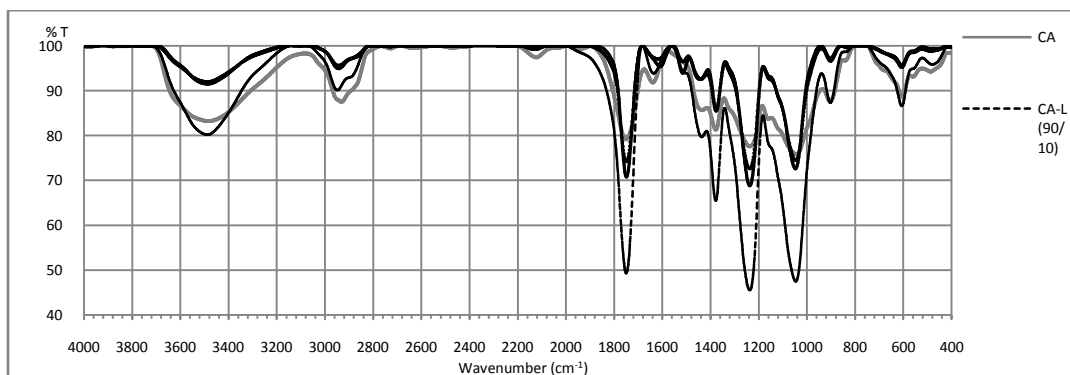

Fig.4 FTIR spectra of CA and CA/L blends

Conclusion

The industrial waste lignin was found to improve the overall thermal stability of CA, though it reduced the initial temperature of decomposition of CA. The CA/L blend of 70/30 composition shows higher T_g, while 90/10 and 50/50 blend composition show lower T_g than CA. The SEM micrographs do not show any phase separation in all the blends. The intermolecular interactions were confirmed between lignin and CA by FTIR analysis.

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