ISSN : 0974 - 7486 Volume 12 Issue 9

Materials Science

An Indian Journal

Full Paper

MSAIJ, 12(9), 2015 [311-316]

Analysis of UV-Vis absorption spectra of luffa cylindrica- resorcinol composites

C.Parida[1]*, S.K.Dash[2], S.C.Das[3]

[1]Depatment of Physics,Orissa University of Agriculture and Technology,Bhubaneswar-751003, Odisha, (INDIA)
[2]Department of Education in Science and Mathematics, National Council of Educational Research and Training,Bhubaneswar-751022,Odisha, (INDIA)
[3]Department of Chemistry, Salipur College, Salipur -754202,Odisha, (INDIA)
E-mail: sivaji_1976@yahoo.co.in

ABSTRACT

This paper dealt with the study and analysis of UV-Vis absorption spectra of treated fibers of Luffa cylindrica (LC), pure matrix and LC fiber-resorcinol composites. The effect of incorporation of LC fiber in to the matrix on the absorption peak is analyzed. The shifting of absorption peak is noticed when the alkali treated LC fibers are incorporated into the matrix. Shifting of the absorbance edge towards low wavelength region for alkali treated LC fiber composites indicate an increase in band gap. The increase in band gap results in decreased optical conductivity of the treated LC fiber composites. Also it is observed that the absorbance peak shifts towards the higher wavelength region with addition of more wt of LC fiber into the matrix. It indicates decrease of band gap and increase of optical conductivity with increase in wt of LC fiber in the composites.

INTRODUCTION

Internal energy of a molecule of any substance is the sum of energy of electrons, energy of vibration between its constituent atoms and energy associated with rotation of molecule. When uv/visible light (200nm to 750nm) passes through the sample, energy from the light is used to promote an electron from ground state into one of the empty anti-bonding orbital. Each wavelength of light has a particular energy associated with it. If that particular amount of energy is just right for making one of these energy jumps, then that wavelength will be absorbed - its energy will have been used in promoting an electron. UV absorption is related to transition between electronic energy levels. The vibrational energy states of various parts of a molecule are much closer than the electronic energy levels and thus photons of lower energy or longer wavelengths (800 nm to 4000nm) are needed to bring change in vibrational energies. Light absorption due to vibrational changes occur in the IR region. Similarly the rotational energy levels of a molecule are so closely packed that light in far IR /microwave region (4000nm to 20000nm) has enough energy to cause the change in rotational energy.

UV-Vis absorption spectroscopy is distinctly unique from the art of spectroscopy. Thus, although it can be used for characterizing certain aspects of group functionality and conjugation, it is not used primarily as a method of qualitative analysis for the identification of unknown compounds.

Absorbance (on the vertical axis) is a measure of the amount of light absorbed. The higher the value of absorbance, the more of a particular wavelength of light is being absorbed. All the molecules of a sample give similar UV-visible absorption spectra - the only difference being that the absorptions move to longer and longer wavelengths as the amount of delocalization of electron in the molecule increases. Therefore absorption needs less energy as the amount of delocalization increases. Thus there must be less energy gap between the bonding and anti-bonding orbital as the amount of delocalization increases.

Natural fibers like LC fibers exhibit colour because its chemical constituents like cellulose, hemicellulose and lignin either reflect, scatter, transmit or absorb light. Because of the light absorption property of natural fibers, a small part of the absorbed energy may be enough sometimes to trigger undesired photo physical and photo chemical processes. Such processes may eventually change the physical, chemical, optical and mechanical properties of materials[1]. In fact, the quantum of energy associated with light in UV range is sufficient to break many of the chemical bonds present in the cellulose, hemi cellulose and lignin. The C-C, C-H, C-O, O-O and O-H linkages may degrade with absorption of UV light. Cellulose present in the LC fiber normally absorbs light energy strongly between 200nm and 300nm. Lignin is the main component in natural fibers which is responsible for colouration of fiber. It shows a strong peak at 280 nm. The combination of UV absorption of cellulose and lignin makes up the absorption spectra of LC fiber[1].

EXPERIMENTAL

The fruit of luffa cylindrica (LC) was collected from local forest area near Barang, Orissa.

The chemicals such as calcium chloride ($CaCl_2$ $2H_2O$, 97%), sodium carbonate (Na_2CO_3, 95%), di sodium hydrogen phosphate (Na_2HPO_4 $2H_2O$, 99.5%), resorcinol ($C_6H_4O_2$), formaldehyde (HCHO), maleic anhydride [$C_2H_2(CO)_2O$], ethylenediamine [$C_2H_4(NH_2)$], sodium hydroxide (NaOH), sodium hypochlorite (NaClO), di-vinyl benzene and methane sulphonic acid all of AR grade were procured from E. Merck, India. De-ionized, doubly distilled water prepared in our laboratory was employed while preparing solvents.

The fibers of LC were cut into small pieces of length around 2cm. These were washed thoroughly with deionized water to remove impurities like oil, dust, part of leaf etc. These are then dried at 70^{o}C in vacuum oven for 20 minutes.

The dried LC fibers are subjected to chemical treatment such as treatment with alkali followed by bleaching and acid hydrolysis, For alkali treatment, the LC fibers were soaked in a 5% NaOH solution at 80^{0}C for 1h. The soaked LC fibers were then washed with fresh water for 30 minutes to remove any excess NaOH sticking to the surface of LC fiber. The fibers were then dried at room temperature for 48 h followed by drying in oven at 60°C for 6h. During alkaline treatment given to the natural fibers the hemicelluloses and lignin present in the natural fibers are extracted. In this way the number of -OH groups present in the fiber is reduced. The decrease in –OH groups increases hydrophobicity of natural fibers which strengthen the bonding between fiber and matrix. There is disruption of hydrogen bonds in the network structure of cellulose due to the alkali treatment. Thus it increases the surface roughness and the adhesion between fiber and matrix. This treatment depolymerizes cellulose and exposes the short length crystallites of cellulose.

The alkali treated LC fibers were bleached with 2% sodium hypochlorite solution. The mixture was continuously stirred for 2h at 80^{o}C. After this the mixture was poured through a filter paper in a funnel. The solid fibers were trapped by the filter paper. After filtration the fibers were washed with distilled water till neutral pH was obtained. The pulp obtained after bleaching is termed usually as micro crystalline cellulose (MCC). The colour of the bleached LC fibers appear yellowish from black. The bleached LC fiber/water suspension was prepared and kept on an ice bath. H_2SO_4 was added slowly under continuous stirring to the suspension placed in an ice water bath, until the final concentration of 60% H_2SO_4 was reached. The obtained suspension was then heated at 45°C under continuous stirring for 2h. In order to remove excess acid the mixture was washed and centrifuged using an ultracentrifuge at 30^{o}C for 20 minutes with 7000 rpm.

Now, the LC fiber modified with CaCl$_2$, were re-immersed in Na$_2$HPO$_4$ solution for 12 h at room temperature to deposit compounds of calcium phosphate over it. Another set of the LC fiber modified with CaCl$_2$ were reimmersed in Na$_2$Co$_3$ solution for 12 h to deposit compounds of calcium carbonate on its surface. Thus two separate sets of modified LC fibers were prepared. One set of treated and untreated LC fibers are modified by calcium carbonate. The other set of treated and untreated LC fibers are modified with calcium phosphate. After 12h the modified LC fibers were washed again with distilled water. The dried fibers were preserved in a dessicator.

Composites are formed by taking RF resin and both chemically treated and untreated LC fibers. Both treated and untreated LC fibers are modified by calcium carbonate and calcium phosphate separately. The prepared grounded RF resin and LC fiber modified with calcium phosphate and calcium carbonate are mixed in different wt proportion. In sample B1 and B2, the matrix and untreated LC fiber are in wt ratio 1 : 1 and 1 : 2 respectively. In sample B4 and B5, the matrix and treated LC fiber are in wt ratio 10 : 1 and 5 : 1 respectively. B3 sample contains only powdered RF matrix and ample C contains only treated LC fiber. The different samples are presented in tabular form in TABLE 3.1. Maleic anhydride (1g) and ethylene di-amine (4.6ml) were added as cross linkers to 1g of resorcinol-formaldehyde resin. The mixture was heated at constant temperature of around 70ºC for 9 h to get composites. After cooling the composite was washed with distilled water, followed by washing in ethyl alcohol to remove monomers present in it. Then composite was allowed to dry for 24h and the dried sample was grounded in to pieces by using mortar and pestle. The grounded composite was then exposed to ultrasonic vibration at 30 kHz for 1 h at room temperature using a sonicator (1.5 L50 H/Deluxe, India). Sonication was responsible to enhance dissolution of particles by breaking intermolecular interactions. The particles of the samples are agitated when exposed to ultrasonic wave and hence particle size decreases. After being sonicated the sample was left dried. 10 g of powdered composites was mixed with 10 g of commercial divinyl benzene and kept for 12 h at room temperature of 28^{0}C. The material was made acidic by addition of 0.25 ml of methanesulphonic acid. The sample was swollen as it absorbed sufficient divinyl benzene in to it. This facilitates the sample to be softened and a paste like material was obtained. This material can easily be shaped and moulded by using mould of different dimensions. The paste was kept in a small mould (10 cm × 2 cm). The mould was heated for 4 h at 60 °C and was cured to get cross linked composite. UV-visible spectral analysis of all the samples were carried out by SHIMADZU UN 2550/JAPAN UV spectrophotometer (Figure 3.9) at room temperature in the wavelength range of 240 nm to 800 nm. The sample was kept in the sample holder. The UV light source was switched on so that the light falls on the sample. The detector detected the remaining UV light that passes through the sample. The processor compared the intensity of original UV light from light source from the detected UV light. The variation of absorbance and transmittance with wavelength were recorded.

RESULTS AND DISCUSSION

The UV spectrum of alkali treated LC fiber in sample C is shown in Figure 1.

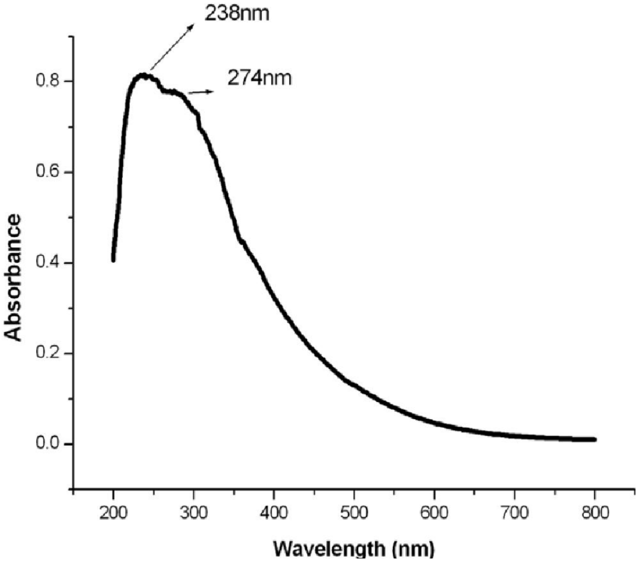

Figure 1 : UV absorption spectrum of alkali treated LC fiber (sample C)

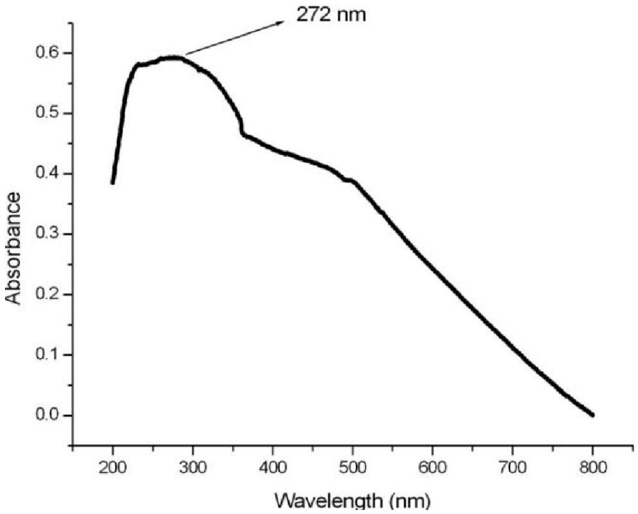

Figure 2 : UV absorption spectrum of resorcinol-formaldehyde matrix (sample B3)

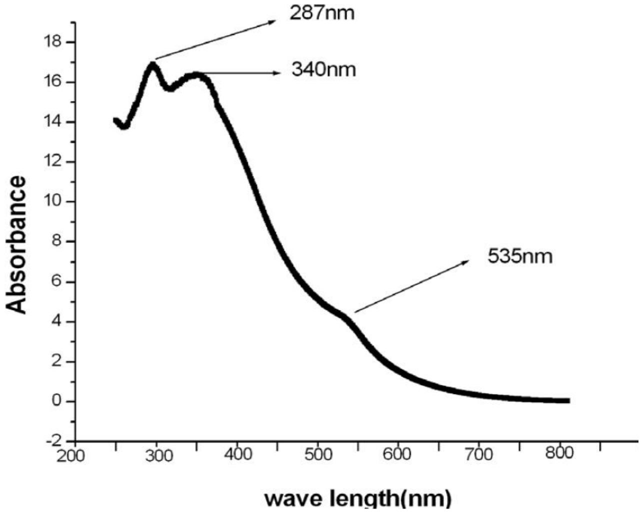

Figure 3 : UV absorption spectrum of untreated LC fiber and resorcinol formaldehyde composite (sample B1)

The UV spectrum does not show any intense peak. The band at 238 nm is due to the absorption of ultra-violet light by cellulose. The peak at 238nm is due to presence of carbonyl group in cellulose structure. The carbonyl group is introduced in to the cellulose structure during the chemical treatment given to LC fiber. A small kink noticed at 274 nm may be due to absorption by cellulose again. Pure cellulose is not a good absorber of light. Mostly lignin contributes to 85% of absorption in natural fibers followed by carbohydrates (10%) and extractives (5%)[1]. As lignin is removed during alkali treatment no strong peak is noticed in the spectrum as shown in Figure 1.

The UV spectrum of resorcinol-formaldehyde matrix is shown in Figure 2. The resorcinol-formaldehyde does not show any intense uv peak. These are yellowish brown in colour and are characterized by a broad absorption peak around 272nm[2]. Due to this absorbance property resorcinol is used in resins as an UV absorber and in manufacturing of fluorescent and leather dyes.

The UV spectrum of untreated LC fiber reinforced resorcinol-formaldehyde composite is shown in Figure 3. The untreated LC fibers are modified with calcium phosphate salts and incorporated into the matrix in the wt ratio 1:1.

As seen from the Figure 3 the composite using untreated LC fiber is characterized by two intense peaks. The peak at 287 nm is due to the contribution of lignin present in the untreated LC fibers[1]. As lignin contributes to 85% of absorption in natural fibers a strong peak is present at 287nm. The peak due to lignin at 287 nm is absent in Figure 1 indicating removal of lignin during alkali treatment of LC fibers. The peak at 340nm in Figure.3 may be due to contribution of cellulose present in the LC fibers. A small kink observed around 535 nm is due to presence of carbonate ion in Ca salts deposited on the surface of LC fibers[3].

Effect of untreated LC fiber loading on UV absorption spectra of composites

The UV spectrum of composite with untreated LC fiber in the matrix in the wt ratio 2:1 is shown in Figure 4. The LC fiber is modified with calcium phosphate.

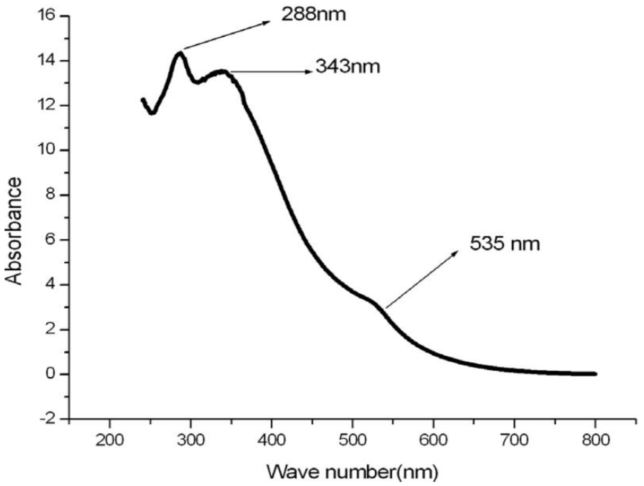

Figure 4 : UV absorption spectrum of untreated LC fiber and resorcinol formaldehyde composite (sample B2)

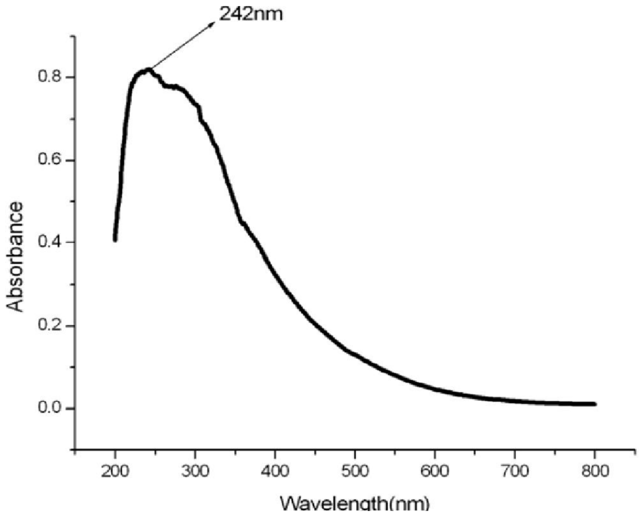

Figure 5 : UV absorption spectrum of treated LC fiber and resorcinol formaldehyde composite (sample B4)

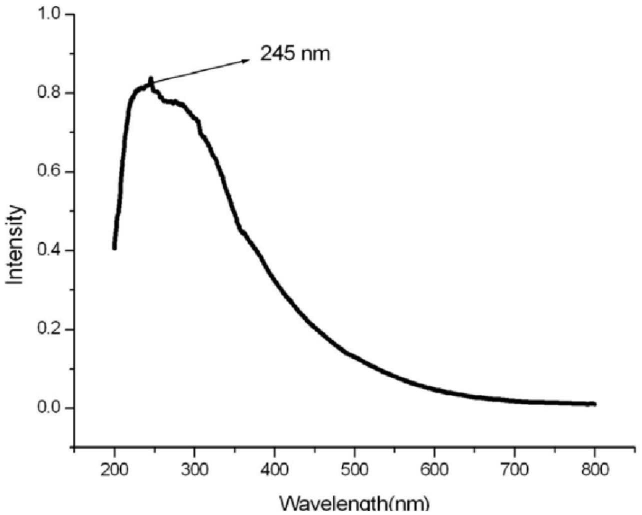

Figure 6 : UV absorption spectrum of treated LC fiber and resorcinol formaldehyde composite (sample B5)

The peak at 287 nm and 340 nm as shown in Figure 3 are shifted to 288nm and 343 nm in Figure 4 respectively. The shifting of peaks towards higher wavelength indicates decrease of band gap energy with increase in wt of untreated fiber in the matrix. When the wt of untreated fiber in the matrix increases it destroys the crystallinity of the composites. With increase in amorphous nature of the composites, amount of delocalization in the molecule increases and the peak shifts towards higher wavelength. With shifting of peak towards longer wavelength decreases the band gap hence increases the optical conductivity of the composites.

Effect of treated fiber loading on UV absorption spectra of composites

The LC fibers are treated with alkali followed by bleaching and hydrolysis. This facilitates the removal of hemicellulose and lignin from the LC fiber. The treated fibers are reinforced into resorci-

TABLE 1 : Characteristic frequencies from UV-Vis spectra

Sample	Nature of the sample	Peaks	Assignment
C	Treated LC fibers	238nm and 274 nm	Cellulose
B3	Resorcinol-formaldehyde matrix	272nm	resorcinol
B1(LC fiber modified with calcium phosphate)	Untreated fiber : matrix = 1:1	287 nm	Lignin
		340 nm	Cellulose
		532 nm	Ca salts
B1(LC fiber modified with calcium carbonate)	Untreated fiber : matrix = 1 : 1	286nm	Lignin
		353nm	Cellulose
		535nm	Ca salts
B2(LC fiber modified with calcium phosphate)	Untreated fiber : matrix = 2 : 1	288nm	Lignin
		343nm	Cellulose
		535nm	Ca salts
B2(LC fiber modified with calcium carbonate)	Untreated fiber : matrix = 2 : 1	286nm	Lignin
		355nm	Cellulose
		537nm	Ca salts
B4(LC fiber modified with calcium phosphate	Treated fiber : matrix = 1 : 10	242nm	Cellulose
B4(LC fiber modified with calcium carbonate)	Treated fiber : matrix = 1:10	243nm	Cellulose
B5(LC fiber modified with calcium phosphate	Treated fiber : matrix = 1 : 5	245nm	Cellulose
B5(LC fiber modified with calcium carbonate)	Treated fiber : matrix = 1 : 5	245nm	Cellulose

nol-formaldehyde for composite formation. The UV spectrum of composites with treated LC fiber in the matrix in the wt ratio 1:10 is shown in Figure 5.

The intense peak present around 287 nm in Figure 4.5.3 and Figure 4 are replaced by a broad peak at 242nm in Figure 5. The absence of peak at 287 nm in Figure 5 signifies removal of lignin during alkali treatment. The peak at 242 nm is due to presence of cellulose in the composite. The pure alkali treated LC fiber was characterized by a peak at 238 nm as shown in Figure 1. When the composites are formed using treated LC fiber, the peak is shifted from 238 nm to 242 nm. The shifting of peak towards longer wavelength indicates delocalization of electrons, decrease of band gap energy and decrease in crystallinity of cellulose. When the treated LC fibers are incorporated into the matrix, there is random distribution of treated LC fibers in the matrix. This generates delocalization and increases the amorphous nature of cellulose. But when the wt of treated LC fibers in the matrix increases, the peak at 242 nm in Figure 5 is shifted to higher wavelength at 245 nm. Again the shift towards higher wavelength indicates decrease in band gap and increase in optical conductivity of the composite. It is shown in the Figure.6 where the LC fiber : matrix wt ratio is 1:5.

TABLE 1 gives the comparison of absorption peaks of treated LC fiber, matrix, composites with treated and untreated LC fibers.

CONCLUSION

The presence of sharp peak at 287 nm in Figure 4.5.4 and 4.5.5 shows that the composites having untreated LC fibers are more optically active compared to the composites using treated LC fibers. The high absorbance of untreated fiber composites is due to presence of lignin in the composites. Lignin is natural UV absorber and ensures protection against UV. When the natural fibers are alkali treated and bleached, the optical absorbance decreases due to removal of lignin. The pure celluloses are pure absorber of light and do not show any intense peak. With the addition of more wt of untreated fiber in to the matrix optical conductivity of the composites is found to increase. The increase in optical conductivity was due to shifting of peaks towards higher wavelengths. With the addition of more wt of LC fiber into the matrix, the peaks are shifted towards higher wavelength (Figure 4). Shifting of peaks towards higher wavelength indicate more delocalization and increase in amorphous behaviour. These results show decrease in crystallinity with increase of wt of untreated LC fiber in the matrix.

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