

Graft Copolymerization of Methymethacrylate on Lignin Produced from Agricultural Wastes

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Abstract

Lignin was isolated from banana pseudo stem, palm frond and coconut husk. The moisture content of the banana pseudo stem and palm frond was determined gravimetrically. The lignin was isolated by alkaline hydrolysis with NaOH followed by precipitation with 72% H₂SO₄. The isolated lignin was then copolymerized with methyl methacrylate via free radical mechanism. The lignin and the corresponding copolymers were characterised by FTIR analysis.

The lignin content in banana pseudo stem, palm frond and coconut husk were respectively 16%, 14% and 13% while the grafting percentage of the corresponding lignin with methymethacrylate (MMA) are 24%, 21% and 19%. These implied that production of lignin from agricultural wastes could reduce the latter solid wastes.

The FTIR analysis of the different lignin showed important peaks such as O-H band between 3433 cm⁻¹ and 3450 cm⁻¹; C=C band around 1515 cm⁻¹ was absent in palm frond lignin; and C=O band was only observed in coconut husk lignin at 1696 cm⁻¹. There was a significant difference in the absorption band of the C-O (ether) of the lignin between 1107 cm⁻¹ and 1198 cm⁻¹. The shift in the absorption peaks in the spectra of the isolated lignin for the different sources of the lignin and the grafting percentage corroborate the fact that the properties and composition of lignin depend on the source of the lignin. The FTIR analysis of the copolymers also showed two prominent peaks for C=O band between 1680 cm⁻¹ and 1708 cm⁻¹; and C-O (ester) between 1220 cm⁻¹ and 1320 cm⁻¹ that were absent in the lignin. These confirm the presence of the acrylate functional groups.

Keywords: banana pseudo stem, palm frond, coconut husk, lignin, agricultural wastes, methymethacrylate

1. Introduction

In the past century, various synthetic polymer materials have been developed in different forms, such as plastics, thermoplastics and synthetic rubbers that are used widely in a variety of fields such as packaging, construction materials, agriculture, and medical devices. Undoubtedly, those synthetic polymer materials perform very important roles in our daily lives. After rapid development for several decades, a Gordian knot is becoming increasingly serious, the continual environmental pollution is caused by non-biodegradable synthetic polymer wastes (Stéphanie and Luc 2014).

Most of the commercial products in the society are fully made of synthetic polymers. However, despite their vast usefulness, their recalcitrant nature eclipses their importance because it is at variance with the concept of green chemistry. Natural polymers which are biodegradable cannot be a direct substitute for synthetic polymers because of some of their properties. In view of this, copolymerization of the side chains of synthetic polymers onto naturally occurring backbones are being considered as a way of producing compounds that are more easily degraded in the environment. Lignin, because of its good physicochemical properties and its enormous abundance offers a promising potential for exploitation.

Lignin, as a class of biodegradable, sustainable, nontoxic and inexpensive natural amorphous hydrophobic branched heteropolymer second only to cellulose in natural abundance, has been widely used for various applications (Chung et al., 2013; Sivasankarapillai and McDonald, 2014). At present, most of lignin is discarded as waste from the pulp and paper making industry (Long et al., 2009).

Lignin is insoluble in water and stable in nature and acts as the glue that connects cellulose and hemi-cellulose. Lignin is a three-dimensional, highly cross-linked macromolecule composed of three types of substituted phenols which are monolignols (coniferyl, sinapyl, and p-coumaryl alcohols) incorporated by enzymatic polymerization yielding a vast number of functional groups and linkages (Boerjan et al., 2003; Carmen et al., 2004; Chakar and Ragauskas, 2004).

The relative amounts of the monolignol units differ considerably between plants. In softwood lignin, the network is formed primarily by coniferyl moieties (95%), the rest consisting of p-coumaryl alcohol-type units and only trace amounts of sinapyl alcohol moieties, while in hardwood and dicotyl crops like hemp and flax, various ratios of coniferyl/sinapyl have been reported (Dence and Lin, 1992).

Lignin cannot be simply removed from growing plants without causing deleterious developmental effects (Bonawitz et al., 2013). Genetic manipulation trials using natural mutants or silencing strategies have failed because they drastically reduced lignin content in a non-selective way. Nevertheless, there are cases in which mild genetic manipulations have been used to moderately reduce lignin content or modify its composition in biomass, modestly improving saccharification efficiency, forage digestibility, and pulping yield (Li et al., 2008).

Lignin from trees, plants and agricultural crops with different chemical composition and properties can be obtained by the use of several extraction methods. Over the last decade, Kraft lignin has been considered for different applications such as replacement of phenol in phenol formaldehyde resins (Mondragon, 2007 and Tejado et al., 2008), vanillin production (Araujo et al., 2010 and Rodrigues Pinto et al., 2011), agent in production of synthetic tannin (Soprano et al., 2005) and utilization as bio sorbents of Heavy metals (Harmita et al., 2009 and Wu et al., 2008) and dyes (Suteu et al., 2009 and Saad et al., 2012).

Graft polymerization is one of the key techniques to covalently modify the surface of lignin by introduction of various functional polymers onto the side chains of lignin, resulting in greatly enhanced mechanical, thermal resistance and UV absorption properties of the host polymers. (Xiaohuan et al., 2014).

This study aimed at isolating lignin from banana pseudo stem, palm frond, and coconut husk all of which are agricultural wastes and copolymerizing the isolated lignin with methymethacrylate to obtain biodegradable products. This production of lignin from these wastes would also conserve its source from wood used for pulp and paper and consequently help in afforestation.

2. Materials and Method

2.1 Materials

The banana pseudo stem and palm fronds were collected from the farm behind the Chemistry Department, University of Ibadan, Ibadan. The coconut husks were purchased from Bodija market, Ibadan, Nigeria. The samples were carefully cut and washed with distilled water.

2.2 Determination of Moisture Content

The moisture content of the banana pseudo stem the palm frond and coconut husk was determined gravimetrically by loss in weight after heating to a constant weight in the oven at 105°C. This was carried out by drying crucibles to a constant weight in an oven at 105°C. Known weights of the samples were weighed into the dried crucibles and then dried to constant weight at this same temperature in the oven. The moisture content is the difference between the weight of the dried crucible with the sample and the weight of the dried crucible. This was carried out for the banana pseudostem, palm frond and the coconut husk.

2.3 Isolation of Lignin

50 g of the dried sample was boiled in 2.5 M sodium hydroxide solution on a hot plate under high pressure for two hours. It was then allowed to cool after which it was filtered with a cloth filter. The pH of the filtrate was adjusted to 3.0 with 72% sulphuric acid. The resulting precipitate was filtered with a filter paper and dried.

The precipitate of the lignin was purified by washing it with ethanol, followed by hot water after which it was dried in the oven and cooled in the desiccator.

The lignin content was determined as follows:

$$\text{lignin content} = \frac{\text{weight of lignin}}{\text{weight of dried sample (50g)}} \times 100\%$$

2.4 Graft Copolymerization of the Lignin and Methyl Methacrylate

The copolymerization reaction was performed as suggested by Xiaohuan Liu (2014). 1.0 g calcium chloride was added to 20 ml dimethyl sulfoxide solvent in a conical flask and then stirred until dissolved. This was followed by the addition of 1.0 g lignin and the solution was stirred for 20 min. 8 ml methyl methacrylate (MMA) was added followed by 1 ml Hydrogen peroxide. After 5 min of stirring, the conical flask was heated on a water bath set at 40°C for 24 hours. The reaction was terminated by the addition of 4.0 mg quinol (4-hydroxyphenol).

After finishing the grafting reactions, the resulting solution was added drop wise to a 20-fold excess of diluted hydrochloric acid solution (pH = 3.0), and the precipitated copolymer was filtered, and repeatedly washed with water.

The final product was dried in an oven at 80°C for 48 h.

The grafting percentage was calculated as suggested by Teena *et al.*, (2010) as follows:

$$\text{Grafting percentage} = \frac{W_2 - W_1}{W_1} \times 100\%$$

Where W_2 = total weight of solid mass recovered from the grafting reaction

W_1 = weight of lignin used.

2.5 Characterization of the Lignin and Its Copolymer Using FTIR

The various lignin and their corresponding copolymers were qualitatively characterized by the FTIR technique. The FTIR spectra of the lignin and copolymers were obtained on a Perkin Elmer Fourier transform infrared spectrometer. The spectra were recorded between 4000-400 cm^{-1} , using KBr as reference.

3. Result and Discussion

The moisture content of the banana pseudo stem and the palm frond are high (Table 1). This is also shown in Figure 1. The coconut husk has negligible moisture content. There was no difference in the weight of the coconut husk after drying in the oven at 105°C. The lignin content is highest in banana pseudo stem as presented in Table 1 and plotted in Figure 2.

Table 1. Physicochemical Properties of the Samples Studied

Sample	% Moisture Content	% Lignin Content on dry basis	Grafting %
Banana Pseudo stem	89	16	24
Coconut Husk	-	14	21
Palm Frond	48	13	19

Values are mean \pm SD for n=3.

The grafting percentage of the various lignin is shown in Table 1. The lignin isolated from banana pseudo stem showed better grafting compared to those obtained from palm frond and coconut husk. This implies that the grafting of lignin is affected by the source since the composition also varies with the source.

The FTIR spectrum of the lignin from banana pseudo stem Figure 4 and tabulated in Table 2 showed important bands such as O-H stretching vibration at 3449 cm^{-1} , C-H stretching vibration (aromatic) at 2925 cm^{-1} , C-H stretching vibration (alkane) at 2851 cm^{-1} , C=C stretching vibration (aromatic) at 1638 cm^{-1} and 1515 cm^{-1} and C-O stretching vibration at 1107 cm^{-1} . This is similar to those observed by Carmen *et al.*, 2004. The stretching frequencies changed in the copolymer.

The changes in the stretching frequencies of O-H, C=C and C-O and appearance of C-O (ester) as observed in the copolymer, CBPSL (Figure 5) suggests the modification of the lignin. The decrease in the stretching frequencies of O-H and C-H (deformation) is due to conjugation and hydrogen bonding in the copolymer. The reduction in the stretching frequency of C=C is due to conjugation. The emergence of the two peaks shown at 1686 cm^{-1} (C=O) and 1229 cm^{-1} (C-O) confirms the presence of the acrylate functional groups.

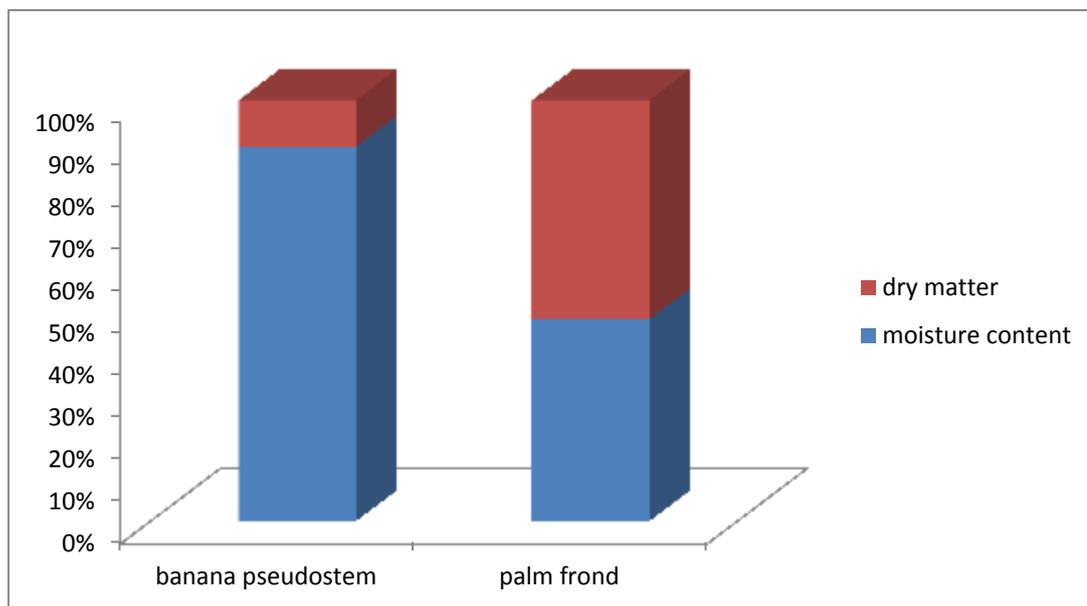


Figure 1. Moisture content of banana pseudo stem and palm frond

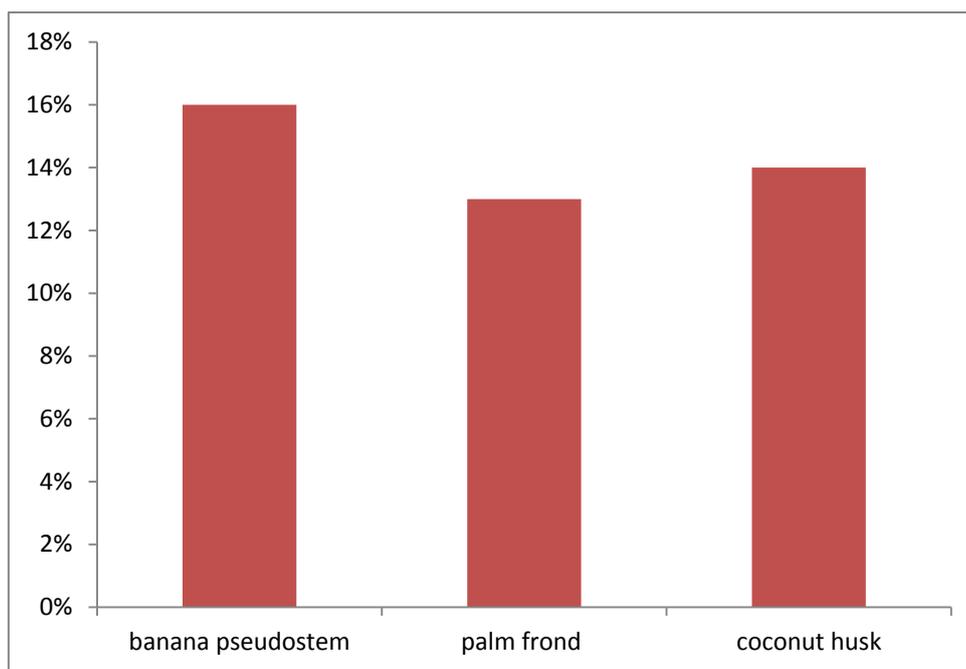


Figure 2. The lignin content of dried banana pseudo stem, coconut husk and palm frond

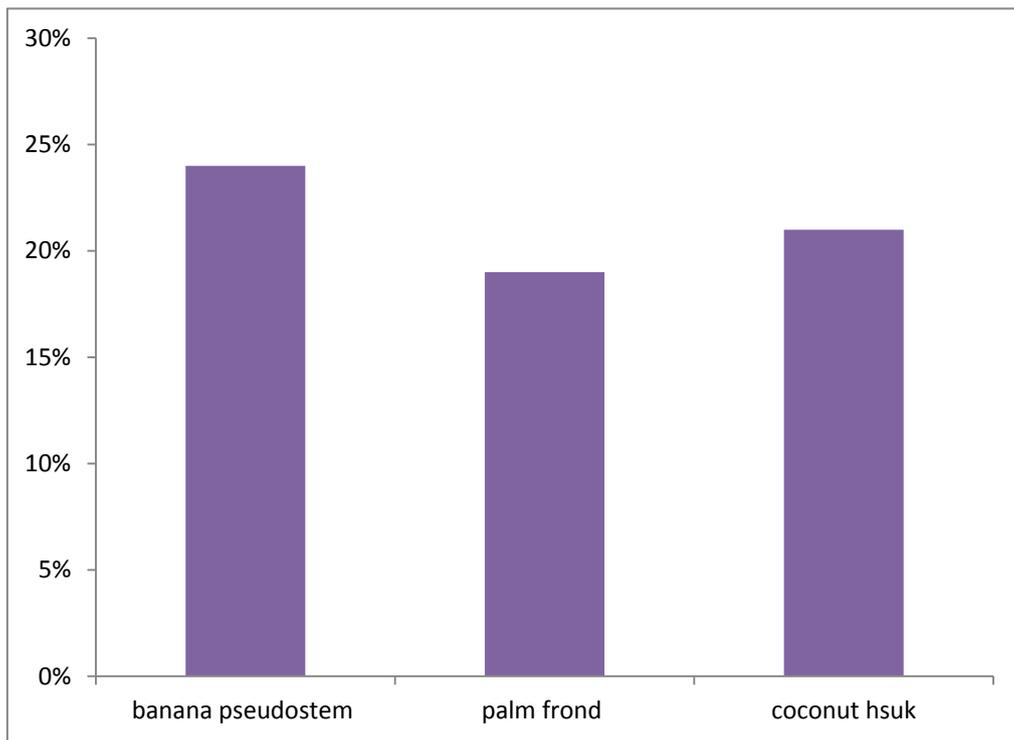


Figure 3. The grafting percentage of the various lignin

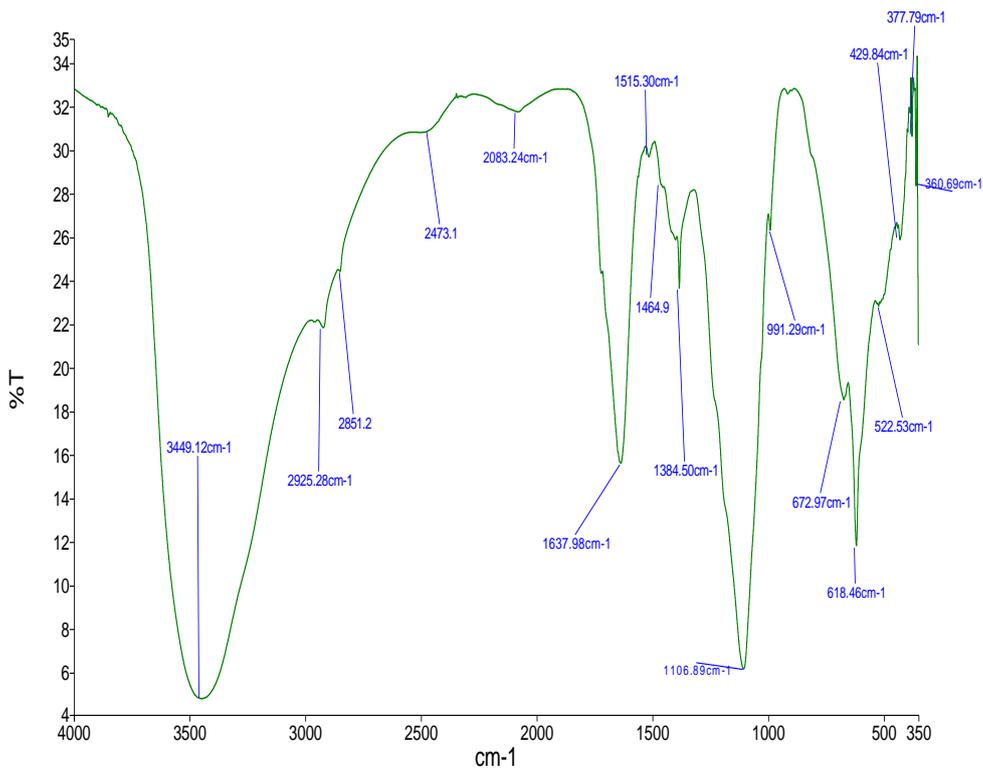


Figure 4. The FTIR spectrum of lignin isolated from banana pseudo stem

Table 2. FTIR of the Lignin from various Sources and their Corresponding Copolymer

Bond Type	Sample Absorption Band (cm ⁻¹)					
	BPSL	PFL	CHL	CBPSL	CPFL	CCHL
O-H stretching vibration	3449	3450	3433	3407	3429	3421
C-H stretching vibration (aromatic)	2925	2922	2924	2921	2919	2921
C-H stretching vibration (alkane)	2851	2851	2852	2851	2850	2852
C=O stretching vibration	--	--	1696	1686	1680	1708
	1638 &		1626 &	1621 &		1615 &
C=C stretching vibration (aromatic)	1515	1637	1514	1508	1621	1514
C-H deformation	1465	--	--	1421	1463	1465
O-H deformation	1385	1384	1389	1384	1384	1384
C-O stretching vibration (ester)	--	--	--	1229	1315	1318
C-O stretching vibration (ether)	1107	1198	1195	1116	--	1123
C-O deformation	--	--	--	1027	--	--

Key: BPSL = banana pseudo stem lignin; CBPSL = copolymer of banana pseudo stem lignin and methlymethacrylate

PFL = palm frond lignin; CPFL = copolymer of palm frond lignin and methlymethacrylate

CHL = coconut husk lignin; CCHL = copolymer of coconut husk lignin and methlymethacrylate

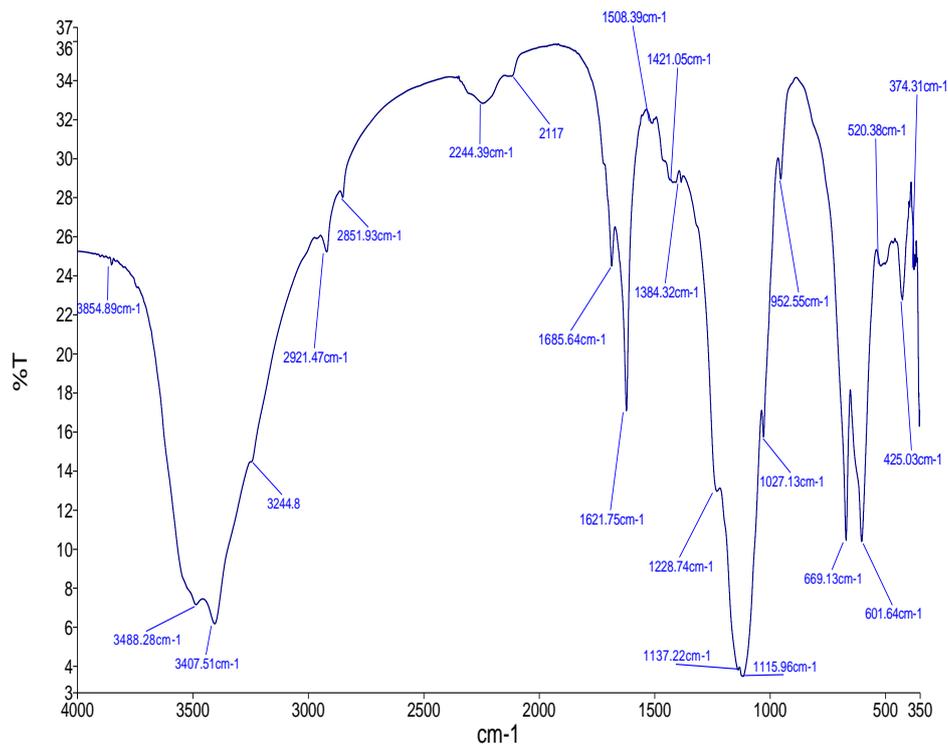


Figure 5. The FTIR spectrum of the copolymer from the lignin isolated from banana pseudo stem and MMA

The FTIR spectrum of the lignin isolated from palm frond (Figure 6) showed important bands such as O-H stretching vibration at 3450 cm⁻¹, C-H stretching vibration (aromatic) at 2922 cm⁻¹, C-H stretching vibration (alkane) at 2851 cm⁻¹, C=C stretching vibration (aromatic) at 1637 cm⁻¹ and C-O stretching vibration (ether) at 1198 cm⁻¹.

The copolymerization of this lignin with methlymethacrylate that produced copolymer CPFL is evident in the changes observed in the spectra (Figure 7) notably in O-H, C-H, C=C, and C-O. The decrease in the stretching frequencies of O-H and C-H is due to conjugation and hydrogen bonding in the copolymer. The reduction in the stretching frequency of C=C is also due to conjugation. The appearance of two important peaks of C=O at 1680 cm⁻¹ and C-O of ester at 1315 cm⁻¹ further confirms the presence of the acrylate functional groups in CPFL copolymer.

The FTIR spectrum of the lignin obtained from coconut husk (Figure 8) showed important bands such as O-H stretching vibration at 3433 cm⁻¹, C-H stretching vibration (aromatic) at 2924 cm⁻¹, C-H stretching vibration (alkane) at 2852 cm⁻¹, C=O stretching vibration at 1696 cm⁻¹, C=C stretching vibration (aromatic) at 1626 cm⁻¹ and 1514 cm⁻¹ and C-O stretching vibration at 1195 cm⁻¹. The stretching frequencies changed in the copolymer.

There were changes in the stretching frequencies of O-H, C-H, C=O, C=C, and C-O in the copolymer prepared from coconut husk lignin and methlymethacrylate (Figure 9). The decrease in the stretching frequencies of O-H and C-H is due to conjugation and hydrogen bonding in the copolymer. The reduction in the stretching frequency of C=C is due to

conjugation. The increase in the carbonyl stretching frequency from 1696 cm^{-1} to 1708 cm^{-1} and the emergence of the peak around 1318 cm^{-1} validates the presence of the acrylate functional groups.

Comparing the spectra of the lignin obtained from the banana pseudo stem, palm frond and coconut husk, it can be inferred that there are slight variations in their structures (Table 2). The slight variation confirms the fact that the properties and composition of lignin depend on the source (Carmen et al., 2004).

The broad band between 3433 cm^{-1} and 3450 cm^{-1} can be attributed to the hydroxyl groups in the phenolic and aliphatic structures. The bands around 2922 cm^{-1} and 2925 cm^{-1} , predominantly arising from the C-H stretching can be attributed to the aromatic methoxyl group and the aromatic moiety. The peaks between 2850 cm^{-1} and 2852 cm^{-1} arise from the C-H stretching in the aliphatic methylene group.

Unlike other lignin isolated, the spectrum of the lignin isolated from coconut husk showed a peak around 1696 cm^{-1} which is characteristic of the carbonyl group. This variance could be due to the source of the lignin. Similar results were recorded by Carmen *et al.*, (2004) and Li Jingjing, (2011). Aromatic skeleton vibrations around 1620 cm^{-1} and 1515 cm^{-1} and the C-O (ether and alcohol) stretching frequencies between 1100 cm^{-1} and 1200 cm^{-1} were also prominent in all the spectra.

The copolymers all show distinctive peaks between 1680 cm^{-1} and 1708 cm^{-1} which is indicative of the carbonyl group. The C-O band between 1220 cm^{-1} and 1320 cm^{-1} was also observed in all the copolymers. This confirms the presence of the acrylate functional groups.

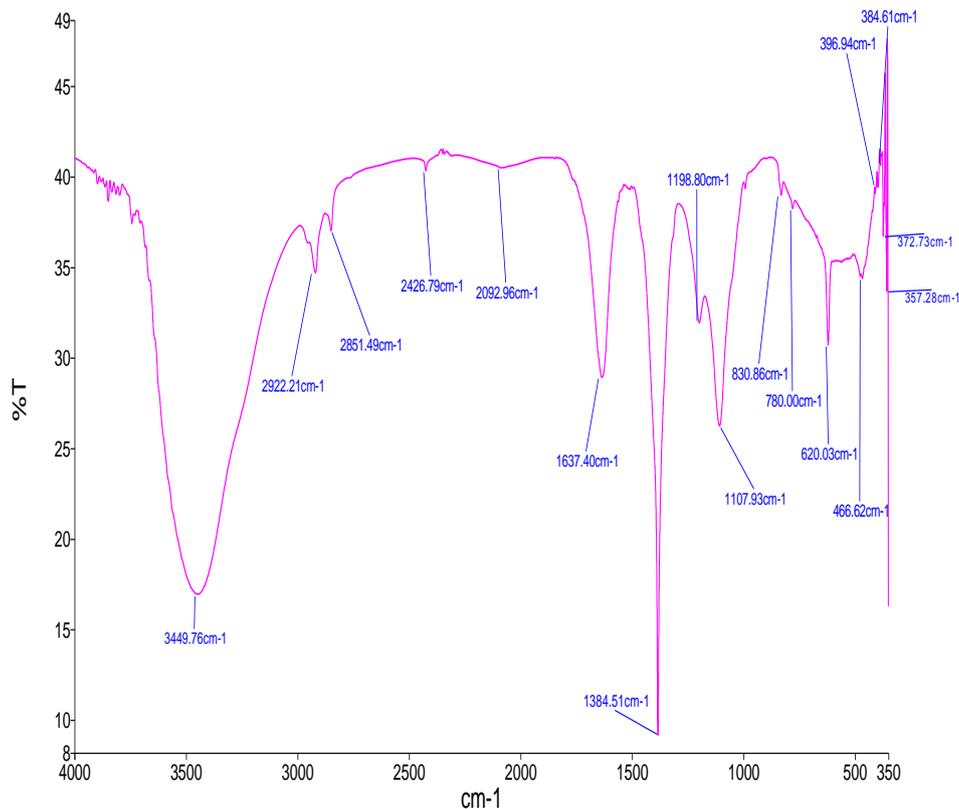


Figure 6. The FTIR spectrum of lignin isolated from palm frond

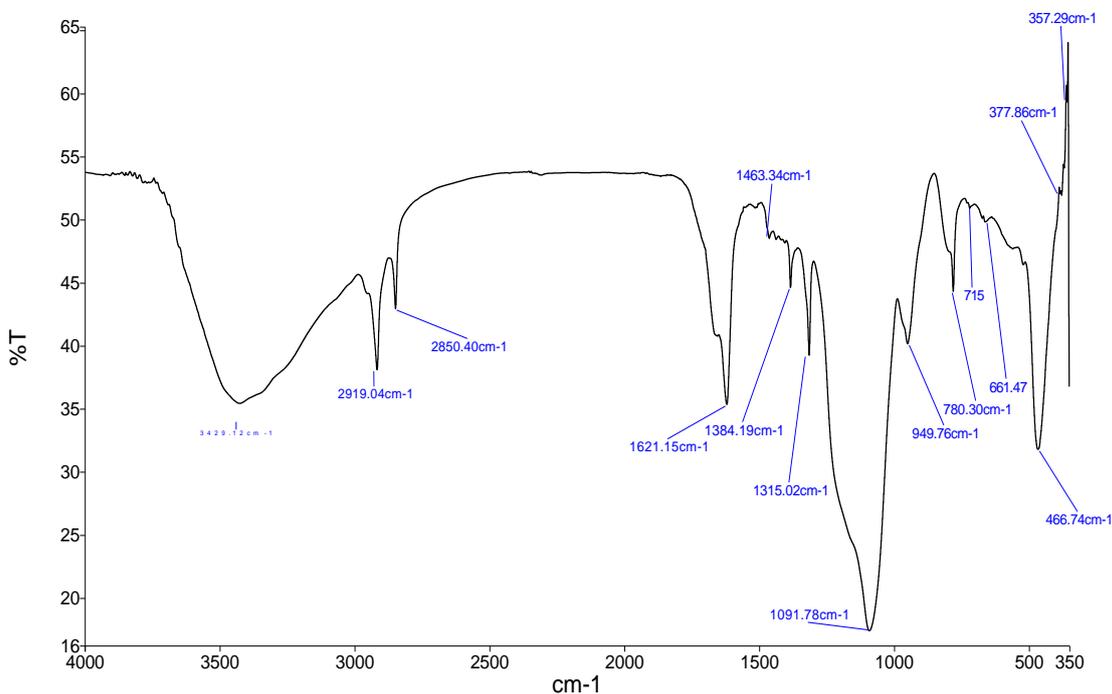


Figure 7. The FTIR spectrum of the copolymer from the lignin isolated from palm frond and MMA

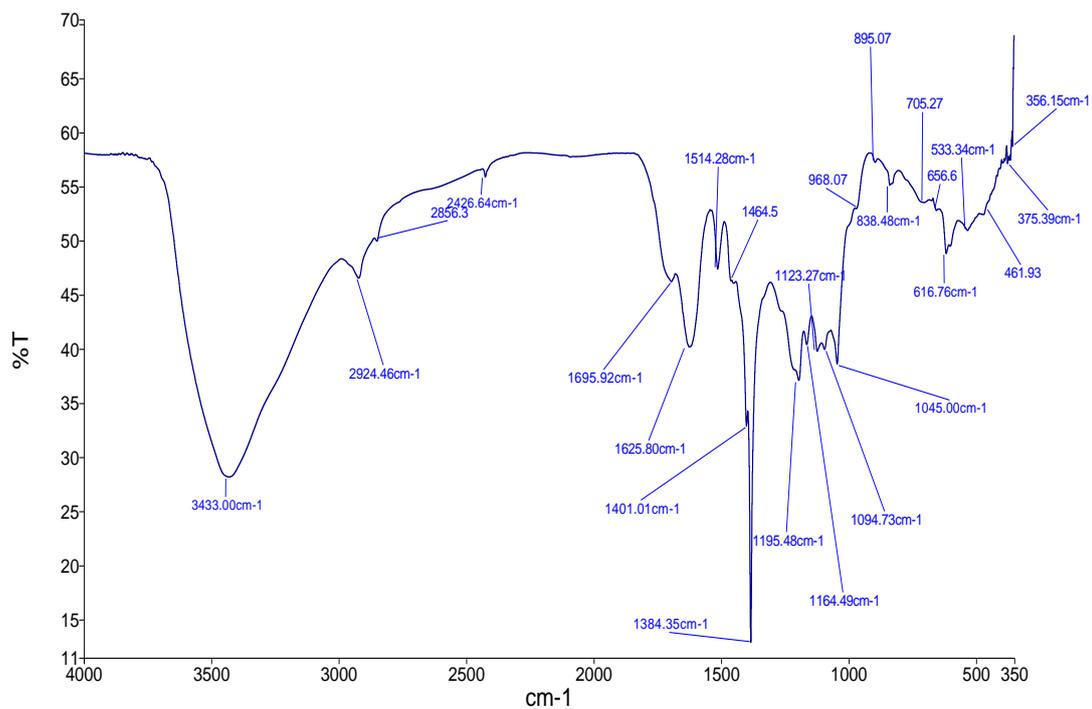


Figure 8. The FTIR spectrum of lignin isolated from coconut husk

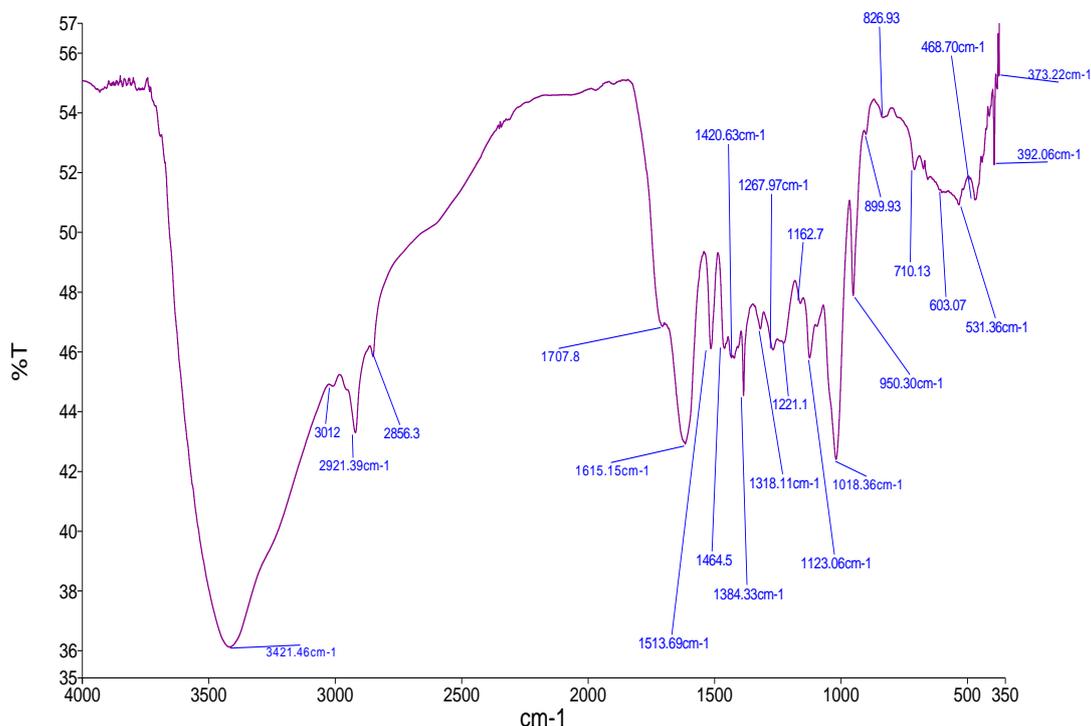


Figure 9. The FTIR spectrum of the copolymer from the lignin isolated from coconut husk

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