

**FTIR STUDIES ON COMPOSITE BLENDS AND BIODEGRADABILITY
PRODUCTS OF GUNA PROTEIN/CELLULOSE BASED
BIOCOMPOSITES**

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ABSTRACT

Composite blends were formulated from guna protein/cellulose based biomaterials. The blends ratios prepared using solution method to produce blends ratios of (90/10 to 0/100). These were subjected to soil burial tests from 20 days through 80 days. FTIR analysis was carried on the composites and degraded blends. The results obtained from FTIR analysis confirmed the degradability of the polymer (guna protein/cellulose) by chemical changes in terms of appearance and shortening of peaks. Remarkably, peaks were newly indicated at 703.06cm^{-1} and 861.24cm^{-1} respectively. These absorption bands were ascribed to C-H aromatic bending and C-H bending respectively. Consistency in peaks at a frequency of 2965.65cm^{-1} ascribed to C-O Group was recorded for all the blend ratios. Aldehyde group stretching at a frequency of 1714.77cm^{-1} was also observed for degraded blends.

KEYWORDS: Biodegradability, FTIR, Guna protein, Cellulose and Composites.

INTRODUCTION

The problems of non-biodegradable plastics waste remains a challenge due to its negative environmental impact. In this sense, biodegradable polymers from natural sources have been receiving much attention lately due to their biodegradability in soil, biocompatibility, environmentally friendly characteristics and above all non-toxicity (3).

Biodegradable composites made entirely from natural materials such as corn, wheat, protein etc, are recyclable and no additional energy is required to break down the materials. However, the commonly used synthetic polymers like polyethylene, polypropylene etc are normally non-biodegradable under environmentally triggered condition and persist for a long creating cycles of waste and waste disposal problems (4). Therefore, uses of green polymeric materials especially renewable polymers and polymer materials are most encouraging from the ecological, economical, environmental protection and as well as resource recycling point of view (5).

Biodegradable polymers derived from renewable source have many functional properties; a remarkable property is recorded in packaging as carry bags for delivery of food stuff, clothes, gifts and other perishable commodities. The uses of plastic shopping bags are now a day to day practice in many countries of the world (5).

Consequently, growing concerns the world over as regards to the persistence of synthetic polymers have generated increased public and scientific interests regarding the use and development of biodegradable polymers as ecologically useful alternative to synthetic polymers which must still retain the desired chemical and physical properties of conventional plastics, thus providing a solution for the existing severe problems of plastic waste. In this regards, cellulose as an abundant biopolymer in the productions of polymeric materials such as load bearing components, fibres and other applications that require stiffness(12). Mixtures can be used as news biomaterials for producing new processable polymeric materials that hopefully possess biocompatibility properties. Polymer blending is designed to produce materials with optimized chemical, structural, morphological, biological as well as mechanical properties (13).

For the reasons mentioned above, there is considerable interest to develop environmentally-friendly, fully biodegradable “green” composites using yearly renewable (sustainable) plant-based fibres and resins (Metravali *et al.*, 2003(14); Nickel *et al.*, 2003(15); Goda *et al.*, 2004(16); Takagi *et al.*, 2002(17); Okuba *et al.*, 2002(18); Yamashita *et al.* 2004(19); Thomas 2004(20) and Lodha *et al.*, 2004(21)).

Results of these investigations revealed that green composites obtained from Guna protein/fabrics and soy protein/yarns are great improvements in terms of mechanical properties as well as the plausibility of using the composites (soy protein/yarn) for secondary structural applications such as door panels and packaging (22). The use of other protein source like soybeans for example with 40% protein content with even at lower functionality of approximately 2.5(23) results indicated increased mechanical properties in terms of modulus suitable for packaging. Guna protein as a biopolymer has 60% (24; 25) protein content over soy beans coupled with reported higher functionality suggests better properties in the finished composites. Greater functionality implies

possibility of better mixing/blending of composites thereby reducing the problems of phase separation, leading to greater improvement in terms of performance and improved properties

FTIR is a dependable tool in the determinations of elucidation of molecular structures and applications. Some researchers (9; 10) have reported the use of FTIR in study of natural polymers and protein material.

Based upon these considerations, FTIR was used to access the molecular interaction of GP/CF composites in their various blends and degradability in various days.

2.0 MATERIALS AND METHODS

2.1 MATERIALS

A plain woven 100% cotton fabric of commercial quality was obtained from the market (Jimeta ultra-modern market). Guna obtained from farm lands in Jimeta.

Assorted chemicals of analytical grade supplied by British drug House (BDH) were used and these included ethanol, acetic acid, potassium dihydrogen phosphate, magnesium sulphate, sodium silicate hydrogen tetraoxosulphate (vi) acid, hydrogen peroxide, and sodium hydrogen. Other materials used included distilled, flower pots and pH meter. Also used was SHUMADZU 8400S fourier transformed infra-red spectrophotomer.

2.2 METHODS

2.2.1 Soil burial test:

The method of (6) was adopted for the biodegradation studies with slight modification in terms the number of days of degradation and environment of degradation of the formulated composites.

2.2.2 Sample Preparation

The method described by (1) as modified by (12) was adopted for the resin preparation. Blends of GPR/CF composite were prepared by firstly blending the modified resin and water in the ratio of 1:10 of Guna protein resin (GPR)/ water to obtain various proportions of the blends of water in the proportions 0/100 to 100/0.

2.2.3 Composite Preparation

Composite samples of various blend ratios that are from 90/10 to 0/100 measuring 10cm by 2.5cm were buried in six different pots filled to their capacities with soils and compost at the depth of 10cm each. The soil was kept in the laboratory and the moisture maintained by sprinkling water at regular interval. Excess water was allowed to drain at the bottom of the pots.

The degradation of the samples was determined at regular interval by carefully removing the samples from the soil and washing with distilled water to remove the soil. These were then oven dried and stored in polythene bags until needed for further analysis. A total of fifty samples were obtained.

2.2.4 Biodegradability Studies

Samples of 10cm in length and 2.5cm (width) were cut and prepared from all the composite composition and prepared in accordance to the method described in section 2 of (ASTMD790).

The composite blends were buried in composted soil obtained from a farmland filled into pots to their capacities. The soil pots containing the samples were kept in laboratory and moisture maintained by sprinkling moisture at regular intervals. The excess water was drained from a hole at the bottom of the pot.

The degradation of the samples was determined at regular intervals of 20 days by carefully removing the samples from the soil and gently washing them with distilled water to remove the soil from the samples. These were then dried in an air oven at 50°C for 24 h. The samples were then kept in polythene bags until needed for further analysis.

2.3 CHARACTERIZATION

Fourier transformed infra-red spectrophotometer (FTIR) SHUMADZU MODEL 8400S with the frequency range 500 to 4500 cm⁻¹ was used to obtain the spectra of the various ratios of the composites blend and degraded composites at NARICT Zaria. The samples were mounted on to the instrument and the frequency and % transmittance were automatically plotted.

3.0 RESULTS AND DISCUSSIONS

3.1 RESULTS

From Table 4.12 the spectral data indicated bands which could be ascribed to C-H, COOH, Amide I and II and ketone and bands ascribed to Amide I, carbonyl, ketone and carboxylic groups registered. Indication of Amide I band was at a frequency of 1600 cm⁻¹ was registered in control. This band was also replicated in composite ratios 40/60 at a frequency of 1621.83 cm⁻¹ and ratio 30/70 at frequency peak of 3550.10 cm⁻¹ indicative of N-H group stretching. A band of C=C stretch was observed on the spectra of composite ratios 20/80 and 80/20 with a frequency of 1693.36 cm⁻¹. There was a band of C=O ascribed to carbonyl stretch in the blends. This is shown in Table 1

Table 1: Spectral analysis of pure composite Blends

Blend Ratio	Spectral Bands (cm ⁻¹)	Tentative Assignment of Band
100/0	1709.85	C=O(Stretch)
90/10	1765.35	C=O(Stretch)
80/20	1693.36	C=O(Stretch)
70/30	3550.10	N-H(Amide)
60/40	1621.83	C=O(Stretch)
50/50	1600.01	N-H(Amide)
40/60	1623.15	C=O(Stretch)
30/70	1600.01	N-H(Amide)
20/80	1693.36	C=O(Stretch)
10/90	1754.21	C=O(Stretch)
0/100	1785.16	C=O(Stretch)

Table 2 represents the FTIR results of degraded composites of various ratios for a period of 20days. From the spectra, indications of carbonyl group stretch at a medium of 1709.85 cm⁻¹ were observed in all the blend ratios. There was the appearance of two new peaks at the frequencies of 860.28 cm⁻¹ and 706.93 cm⁻¹ in all the blends ascribed to aromatic bending and C-H bending respectively. A peak of high intensity of 2956.69 cm⁻¹ ascribed to CH₂ stretch was also observed in the sample blends. There was peak at 1713.61 cm⁻¹ ascribed to carbonyl group or ketone group in all the blends. The intensity of these peaks were however reduced peaks due likely to protein dispersed on the surface of the cellulose material.

There was a peak at 1033.36 cm⁻¹ which could be ascribed to C-H group alkane stretch in the blend ratio 50/50 and also in the ratio 0/100 double peak at increased intensity of 1117.29 cm⁻¹ which was also ascribed to C-H. This shown below in Table 2

Table2: Spectral Analysis of Degraded blends Buried for 20days

Blend ratios	Spectral Bands (cm ⁻¹)	Tentative Assignment of Bands
100/0	1706.39	C=O(Ketone Stretch)
	1028.39	C-O(Ketone Stretch)
	846.97	C-H (Bending)
	1396.44	O-H(Bending)
	2956.01	CH ₂ (stretch)
90/10	1712.85	C-H(Stretching)
	864.14	C-H(Stretching)
	1713.61	C=O(Stretching)
80/20	1713.61	C=O(Stretching)
	794.70	C-H(Stretching)
	1117.29	C-H(alkane stretch)
70/30	1713.61	C=O(Stretching)
	793.73	C-H(Stretching)
	854.49	C-C(Stretching)
60/40	1713.61	C=O(Stretching)
	849.67	C-C(Stretching)
50/50	1033.36	C-O(stretch)
	1713.61	C=O(Stretching)
40/60	849.67	C-H(Bending)
30/70	862.50	C-H(Bending)
20/80	862.50	C-H(Bending)
10/90	862.50	C-H(Bending)
0/100	862.50	C-H(Bending)

The FTIR spectra of samples subjected to burial period of 40days is shown in Figure 1. From the figure, an indication of two new peaks at a reduced intensity of 695.36cm⁻¹ and 861.24cm⁻¹ which could be ascribed to aromatic C-H stretching and C-H bending respectively. There was a medium band at 1713.81cm⁻¹ in samples ratios 70/30, 40/60 ascribed to carbonyl group stretching. Likewise, a high intensity band at a frequency of

2970.46cm⁻¹ ascribed to carboxylic carbonyl stretch observed on composite samples of 70/30 and 40/60.

Table 3: Spectral Bands of Degraded Blends Buried for 40days

Blend ratios	Spectral Bands	Tentative Assignment of Bands
100/0	1034.34	C=O(Stretch)
	1435.09	C-H(Bending)
	2929.00	CH ₂ (Stretch)
90/10	1714.71	C=O (Ketone Stretch)
	1117.79	C-H (Bending
	704.04	C-H(Bending)
	863.17	C-H (Bending)
80/20	1702.92	C=O (Ketone Stretch)
70/30	863.17	C-H (Alkane Stretch)
	704.04	C-H (Stretching)
	1714.77	C-H (Bending)
	1117.79	C=O (Ketone Stretch)
60/40	1704.29	C-H (Alkane Bending)
50/50	1707.06	C-H (Alkane Stretch)
	1033.86	C=O (Ketone Stretch)
	864.14	C=O (Ketone Stretch)
	1712.85	C-H (Alkane Stretch)
40/60	1114.59	C-H (Alkane Bending)
	1031.95	C=O(Ketone Stretch)
	865.49	C-H (Akane Stretch)
	1713.81	C-H (Bending)
30/70	1113.83	C=O(Ketone Stretch)
	1593.25	C-H (Alkane Stretch)
	1029.08	C-O (Stretch)
	695.36	C-H (Stretching)
20/80	861.24	C-H (Bending)
	803.17	C-H (Bending)
	704.04	C-H (Stretching)
	1024.24	C-H (Alkane Stretch)
10/90	1117.79	C-O (Stretch)
	1714.71	C=O (Ketone Stretch)
	694.90	C-H (Stretching)
	862.21	C-H (Bending)
0/100	1715.74	C=O(Ketone Stretch)
	1580.36	N-H((Amide Bend)
	1110.07	C-H (Akane Stretch)
	1708.90	C=O(Ketone Stretch)

Table 4: Spectral Analysis of Degraded Blends Buried for 60days

Blend Ratios Bands	Spectral Bands (cm ⁻¹)	Tentative Assignment of
100/0	1709.85	C=O(Amide Stretching)
	854.49	C-H(Bending)
	603.38	C=O(Ketone Stretch)
90/10	1034.64	C-O (Stretching)
	1435.09	C=C (Aromatic Ring Stretch)
80/20	784.70	C-H (Stretching)
	854.49	C-H(Bending)
	1114.09	C-H (Alkane Stretch)
	1710.82	N-H (Amide Stretching)
70/30	704.04	C-H(Stretching)
	803.17	C-H (Bending)
	1117.79	C-H (Stretching)
60/40	854.26	C-H (Alkane Stretch)
	603.39	C=O (Ketone Stretch)
	1116.75	C-H (Stretching)
	1705.85	C=O (Ketone Stretch)
50/50	1036.81	C-O(Stretch)
40/60	1715.74	C=O (Ketone Stretch)
	703.39	C=O (Ketone Stretch)
	861.24	C-H (Alkane Bending)
	1112.95	C-H (Alkane Stretch)
	702.11	C-H (Stretching)
30/70	860.29	C-H(Alkane Bending)
	1714.77	C=O(Ketone Stretch)
	1025.20	C-O (stretch)
	1034.64	C=O(Ketone Stretch)
20/80	1711.80	C=O(Ketone Stretch)
10/90	1114.69	C-H (Alkane Stretch)
	802.41	C-H(Bending)
	678.00	C-H(Plane Stretch)
	1709.95	N-H(Amide Stretching)
	855.45	C-H (Bending)

Table 4 above shows the FTIR spectra data of degraded composite samples ratios 100/0 to 0/100 buried for 60 days. From the figures, a peak of 1711.68cm^{-1} for ratio 40/60 and on 0/100 ratio at a wavelength of 1714.77cm^{-1} ascribed to amide N-H group stretch was detected.

A frequency band at the frequency of 2965.65cm^{-1} was observed which is present in other sample ratios investigated and could be ascribed to C=O stretch. Two new bands of frequency 703.06cm^{-1} ascribed to C-H aromatic stretch and 861.24cm^{-1} ascribed to C-H bending were mostly observed in the entire blends.

There was a band at 1714.77cm^{-1} which could be ascribed to amide N-H group stretch and a sharp peak at 2965.65cm^{-1} ascribed to C=O stretch was observed in all the samples. A further observation showed two new peaks at 703.06cm^{-1} ascribed to C-H aromatic stretch and the other at 861.24cm^{-1} ascribed to C-H ring bending was observed in the entire samples.

The extracted spectral bands of biodegraded composite samples ratios 100/0 to 0/100 for 80 days are shown in Table 4 below.

From Table 5, it was observed that there was an appearance of a new peak at a frequency of 1110.01cm^{-1} which could be ascribed to C-O stretch on the blend ratio 40/60. Also a band at 2960.83cm^{-1} ascribed to O-H stretching was observed.

A peak at 1714.71cm^{-1} ascribed to C=O ketone was observed. There was a consistent appearance of two new peaks of weak intensity at 706.93cm^{-1} and 853.53cm^{-1} ascribed to C-H aromatic stretch and C-H alkane bending respectively in composite ratio 30/70.

New peaks at 2111.16cm^{-1} and at 2263.54cm^{-1} ascribed to C-H alkane stretch were also observed in the entire blends .This is shown in table 5.

Table 5 Spectral Analysis of Degraded Blends Buried for 80days

Blend ratios of Bands	Spectral Bands (cm^{-1})	Tentative Assignment
100/0	1715.74	C=O(Ketone stretch)
	859.39	C-H(Alkane stretch)
	703.86	C-H(Bending)
90/10	1713.81	C=O (Ketone Stretch)
80/20	1713.81	C=O (Ketone Stretch)
70/30	1714.77	C=O (Ketone Stretch)
	703.93	C-H(Stretching)
	853.53	C-H(Stretching)
60/40	1712.85	C=O (Ketone Stretch)
50/50	1035.85	C-O(Stretch)
40/60	1712.85	C=O (Ketone Stretch)
30/70	1711.80	C=O (Ketone Stretch)
20/80	849.67	C-H (Bending)
	673.16	C-H (Stretch)
	1711.36	C=O(Stretch)
	1116.03	C-H (Alkane Stretch)
	847.74	C-H (Bending
	679.93	C-H(Stretching)
10/90	1727.31	N-H (Amide Stretching)
0/100	1712.85	N-H (Amide Stretching)
	1116.62	C-H(Alkane Stretch)
	1025.20	C-H(Alkane Stretch)

In all the spectral data, the degradation of GP/CF composites is indicated by the band intensity corresponding to C-H bending deformational vibrations in CH_3 groups ($(1714, 802.41\text{ cm}^{-1})$).The intensities of C=O stretch show decrease after biodegrading ($1785, 1713.81\text{ cm}^{-1}$). The changes in the C=O band are associated with changes in the number of carboxylic end groups in the polymer chain during hydrolytic degradation as well as

cycles of microbial attack (7). There was also a shift in intensity to a higher wavelength of N-H group ($1600, 1714.71 \text{ cm}^{-1}$) structure which is also reported by (8). The changes in the number of carboxylic groups that may have resulted from the changes in C-H stretching as the days of degradation slightly increased. This indicates that the cellulose may have ruptured, therefore paving the way for organisms to attack the chain easily (9); 1). Two peaks which were originally present ($861.24, 703.39 \text{ cm}^{-1}$) characteristics of plane stretch and bending respectively slightly increased as the days of degradation.

In contrast to un-degraded blends, the degraded blends, showed bands at 1026 to 1038 cm^{-1} (C-O stretching /side-chain vibrations) as clarified by the following; in 20 days of degradation (50/50 blend at 1033.36 cm^{-1}) in 40 days of degradation (50/50 at 1033.86 cm^{-1} , 30/70 at 1029.08 cm^{-1} and 20/80 at 1024.24 cm^{-1} respectively), in 60 days of degradation (50/50 at 1036.81 cm^{-1} , 30/70 at 1025 cm^{-1}) and lastly at 80 days of degradation in the blends (50/50 at 1035.35 cm^{-1} , 0/100 at 1025.20 cm^{-1}). The shifts in most peaks towards higher wave-numbers may signify the shortening of polymer bonds finally leading to rupturing of polymer composite bonds. Thus, the FTIR studies of the neat and buried samples suggest strongly that some chemical changes have occurred in some cases indicative of microbial attack and therefore samples prepared are amenable to biodegradation although more work is required.

CONCLUSION

Collecting the above results of the investigations carried out on the GP/CF composite, the following conclusions could be made:

- (i) The FTIR measurement for neat blends have been observed to show peaks at the wavenumbers of ($1785-1715 \text{ cm}^{-1}$), which signifies the formation of esters between the O-H groups of cellulose and COOH of the Guna protein, showing not only physical but also chemical changes. These values however, increased in blends as the compositions and days of burial tests were varied.
- (ii) The increase of peaks of ($1714.71-1600 \text{ cm}^{-1}$) in pure blends and subsequently in degraded blends also signifies degradation.

(iii) Chemically modified biomaterial Cellulose, used in this research work has enhanced biodegradation of biocomposite produced that is CF/GP composite. The results in this study therefore demonstrated the efficiency of the modification of cellulose as an efficient means in enhancing biodegradability

(ii) The biopolymers used in this research work can be harnessed in sustainable manner for composite production. It has been reported that the use of biopolymers in composites production is of great advantage over conventional or fossil based sources. This is due to the fact that the plant (*Citrillus vulgaris*) is an all year crop grown in most parts of the north and west of Nigeria and even neighbouring countries and states.

The development of biocomposite in a sustainable manner is still a grey area in the research community. If the technology is to be put to use, then the main focus of biocomposite is the biodegrading of both the matrix and the reinforcement phases. This together with compatibility of the matrix phase and reinforcement observed in this work leads to the success of producing a complete biodegradable composite as observed in the final product.

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