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Analytical Characterization of Microcrystalline Wood Charcoal Reinforced Polyester Composites Using ED-XRF, FTIR and SEM-EDS Techniques

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ABSTRACT

Various weight fractions (ranging from 0 to 30 wt percent, at 5 wt percent intervals) of microcrystalline wood charcoal powder (75µm) were used to generate polyester-based particle reinforced composites. The developed wood charcoal (WC) particles reinforced polyester matrix composites were successfully characterized quantitatively, qualitatively, and functionally using an energy dispersive x-ray spectrophotometer (EDXRF), scanning electron microscope (SEM) enhanced with ancillary EDS for elemental identification capability and Fourier transform infrared spectrometer (FTIR). Fe_2O_3, CaO, CuO, ZnO and Iron, calcium, copper, zinc are the major oxides and elements discovered in wood charcoal by EDXRF. The characteristics of reinforced polymer composites were found to be improved by these elements and oxides. The key elements revealed by EDXRF analysis were also validated by EDS elemental mapping. SEM images demonstrated that composites supplemented with microcrystalline wood charcoal had high interfacial adhesion and interlocking due to even dispersion of the filler particles. FTIR functional characterization indicated interactions of the microcrystalline wood charcoal fillers with the polyester matrix molecules as modest shifts in the frequency bands of functional groups commonly found in unsaturated polyester resin.

1. INTRODUCTION

Because of the ever-increasing demands of today's current and new technologies on high product capabilities, functions, and performance, monolithic materials are becoming less common in numerous technical sectors (Edoziuno et al., 2021). Several materials can be combined in a natural or synthetic way to create materials with improved qualities and performance. Wood for instance, is a natural composite made up of cellulose (wood fibers) strongly held together by a matrix of lignin. Most structural and functional composite materials used today are man-made and composed of two or more component parts that are macroscopically combined, but does not form soluble mixture (Lakshumu Naidu & Kona, 2018; Madhukiran et al., 2018). In the second constituent, the matrix phase, one constituent known as the reinforcing phase is introduced. Two frequently used approaches for classifying composite materials, the one based on the reinforcing geometrical dimension (which could be particle, flake, or fiber reinforced composites) and the other based on the type of matrix material employed (the matrix could be metallic, ceramic, polymeric or carbon material)

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(Akaluzia et al., 2020). Polymer matrix composites (PMCs), have comparatively high strength, low cost and simple processing routes, thus, they are the most widely used composite materials (Omah et al., 2018). Low service temperatures, high moisture absorption, enhanced thermal expansion coefficients, and low directional elastic characteristics are some of the reasons for their limits in specific applications. During the design and development process, composite materials can be tweaked or tailored to improve their qualities and expand their uses (Durowaye et al., 2018; Jagadeesh et al., 2019; Mochane et al., 2019; Ratna Prasad & Mohana Rao, 2011). Selection of appropriate components, component modification, and composite interface engineering are all strategies for tailoring composite materials. The reasons for tailoring in composite materials is to obtain a trade-off in properties' requirement for specific applications (Afdzaluddin et al., 2021; Paszkiewicz et al., 2020).

The emergence of modern rapid analytical techniques and equipment has made it possible to study the nature, structure and composition of natural and synthetic materials. Materials characterization can be accomplished using a variety of analytical techniques and equipment (Srinivas et al., 2017). On the material to be examined, most of these accessible materials characterization techniques and instruments use probe photons, electrons beams, or ions. To obtain the analytical information, the interaction of these probe beams with the material or the changes produced on the intensity, energy level, and angular distribution of the beam are monitored and measured. The ions, electrons, or photons emitted from the sample under probe beam bombardment may be examined in various procedures. Only one element of the produced alterations could be identified using a particular analytical technique, such as the amount of incident light absorbed or the kinetic energy level and distribution of expelled electrons. In many instances, numerous interrelated processes are at work at the same time. Chemical composition data (oxide or elemental analysis), chemical state and properties, phase identification, and structural determination are among the types of information offered by these procedures (such as length of bonds, atomic lattice sites, and angles).

Common analytical techniques and equipment for quantitative, qualitative and functional chemical characterizations of composites materials include: Energy dispersive X-ray fluorescent spectroscopy (EDXRF), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope with supplementary energy dispersive x-ray spectroscopy detector (SEM-EDS) (Spiegelberg, 2009; Spiegelberg et al., 2016; Srinivas et al., 2017). Infrared spectrometry equipment is an effective tool in analytical laboratories for determining the presence of characteristics molecular functional groups. The relative IR absorbance or transmittance of a substance is plotted against the appropriate vibrational frequency in an infrared (IR) spectrum. When IR radiation is absorbed or transmitted by a substance, its energy is transformed into atomic vibrations. The energy absorbed/transmitted by an atomic bond can result to a change in the length of the bond, regarded as stretching or a displacement in bond angle, a phenomenon known as bending. These stretching and bending phenomena vibrate at a specific frequency depending on the stiffness of the bond and mass reduction of the bonded atoms or functional groups (Burns, 2016). Verification and evaluation of chemical components and impure elements are also indispensable in materials analysis. Hence, elemental quantification and oxide analysis using energy dispersive X-ray fluorescent spectroscopy (EDXRF) with high reliability rank first for this kind of analysis. SEM is commonly employed for high field resolution morphological examination of materials. SEM could be equipped with elemental characterization capability by the

attachment of an EDS detector. These instrumental techniques were used in the current study to conduct the chemical states and composition characterization of unsaturated polyester based composites with microcrystalline wood charcoal particle reinforcement.

2. MATERIALS AND METHODS

2.1. Preparation of Wood Charcoal Reinforcement Materials

Dry lumps of wood charcoal obtained locally were pulverized using a grain-milling machine. Standard BSS 200 sieve size was used for sieving the milled wood charcoal fillers to obtain microcrystalline particles of 75 μm size.

2.2. Development of Wood Charcoal/Polyester Composites

The open mould approach was used to generate the wood charcoal (WC) particles reinforced polyester composites in a progressive manner. The volume of the polyester resin and the microcrystalline wood charcoal fillers were adjusted to provide each sample a total composite volume of 98.21cm^3. The quantities of polyester matrix and wood charcoal filler required were measured using a calibrated glass cylinder and an electronic weighing scale, respectively. To avoid filler agglomeration and promote faster and more homogeneous blending of the reinforcement particles in the matrix, the measured matrix and reinforcement materials were mixed in a 200ml beaker and stirred for 10 minutes with a long glass rod. The catalyst, methyl-ethyl-ketone peroxide (MEKP), was introduced using a disposable syringe at a volume ratio of 0.2ml catalyst to 10ml polyester resin and swirled continuously for two minutes. Another disposable syringe was used to inject the accelerator, cobalt naphthanate, in a volume ratio of 10ml polyester resin to 0.1ml accelerator, and the mixture was agitated for another two minutes. After that, the composite mixture was carefully poured into the prepared wooden molds for various test specimens, and they were allowed to cure for 24 hours before being removed from the molds. Before pouring, a petroleum jelly release agent was put to the wooden mold to make it easier to remove the composites from the molds. Six different weight fractions (5, 10, 15, 20, 25 & 30wt. %) of the WC reinforcements were used to develop a total of six composite compositions as well as the unreinforced polyester matrix.

2.3. Functional Characterization

Agilent Technologies' Cary 630 FTIR scientific instrument was used to analyze the FTIR of produced composites. During the Fourier transform infrared spectroscopy (FTIR) analysis, the spectra were recorded using the transmittance method, and the FTIR spectrum was acquired in the region of 650 – 4000 cm^{-1} wave number with an 8cm^{-1} resolution. It was able to determine the chemical bond information (functional groups).

2.4. Chemical Composition Analysis

The elemental and oxide content of the wood charcoal was quantitatively examined and analyzed using the XRF technique. A "Minipal 4" EDXRF spectrophotometer model, capable of detecting elements lying between the atomic numbers of sodium (Na, Z = 11) and Uranium (U, Z = 92) with high resolution and fast analysis was used in this case.

2.5. SEM-EDS Examination

Etching of the prepared composite samples was carried out at room temperature for about 10s in HNO_3 and HF solution, mixed in a volume ratio of 1:12, and then examined using a Phenom Pro X Model SEM (Phenom world, Eindhoven, Netherlands) equipped with an EDS detector, which gives the SEM analytical capabilities. To boost the electrical conductivity of the SEM samples, they were placed on a conductive carbon impression created by the adhesive tape and coated for 5 minutes. An accelerating voltage of 15 kV was used to scan the samples. The SEM

image is electronically sent to an EDS detector with appropriate elemental mapping software, for automatic identification and quantification of the primary, secondary, and trace elements in the polyester composite samples.

3. RESULTS AND DISCUSSION

3.1. Wood Charcoal Filler Characterization by XRF Method

The EDXRF spectrometer was employed to ascertain the elemental and oxide chemical composition of the microcrystalline wood charcoal filler. In wood charcoal powder, high peaks of calcium, iron, zinc, and copper can be seen in Figure 1.

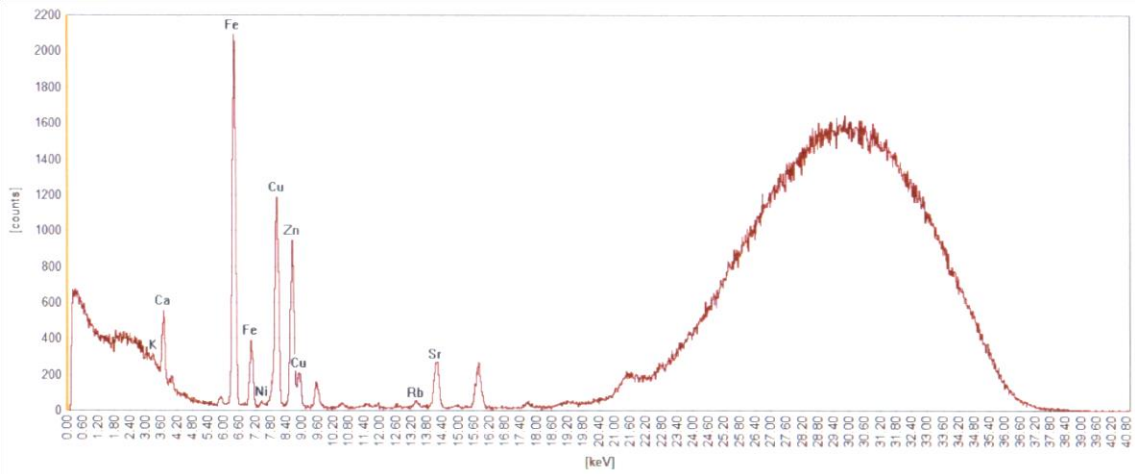

Figure 1. The chemical constituents of microcrystalline wood charcoal as shown in XRF spectra.

The presence of high quantities of these elements was also confirmed by the oxide analysis in table 1. It is opined that the presence of high peaks of these hard metal oxide should improve the mechanical characteristics of microcrystalline wood charcoal reinforced polyester composites. As a result, it is increasingly used as a particle reinforcement for composites based on metal and polymer matrix.

3.2. Functional Analysis by Infrared Radiation (FTIR)

For ease of comprehension and presentation, the vibrational frequency of an IR photon is generally translated to wavelength and then inverted. A wavenumber (λ) is a unit of measurement that is symbolized by cm-1. The infrared spectrum is divided into three distinct regions: far infrared (0-400 cm-1), mid infrared (400 – 4,000 cm^{-1}), and near infrared (4000-14,285 cm^{-1}) (Burns, 2016). The mid-infrared range contains a substantial percentage of molecule structure information and functional groups for most practical applications. The near- and far-infrared areas provide specialized information such as lattice vibrations. There are four spectrum sections in the mid-infrared region: the fingerprint region (400-1500 cm^{-1}), the double bond region (1500-2000 cm-1), the triple bond region (2000-2500 cm^{-1}), and the X—H stretching region (2500-4000 cm^{-1}). The FTIR operator uses the signals that emerge in these to identify most molecular structures, functional groups, and organic bonds by comparing them to the infrared correlation chart

Table 1: XRF oxide analysis results for wood charcoal reinforcement.

Compound (Oxide)	Peaks (cps/mA)
CaO	4369
Fe_2O_3	3456
CuO	2017
ZnO	1646
SiO_2	531
Al_2O_3	496
MgO	123
P_2O_5	308
TiO2	173
MnO	439
K_2O	724
WO_3	52
SrO	33
ZrO_2	22
BaO	21
V_2O_5	15
Cr_2O_3	12
Na_2O	5
Rb_2O	5
Ga_2O_3	4
PbO	2
As_2O_3	1
Y_2O_3	1
Ni_2O	12
Nb_2O_5	0

(Adediran et al., 2021; Burns, 2016).

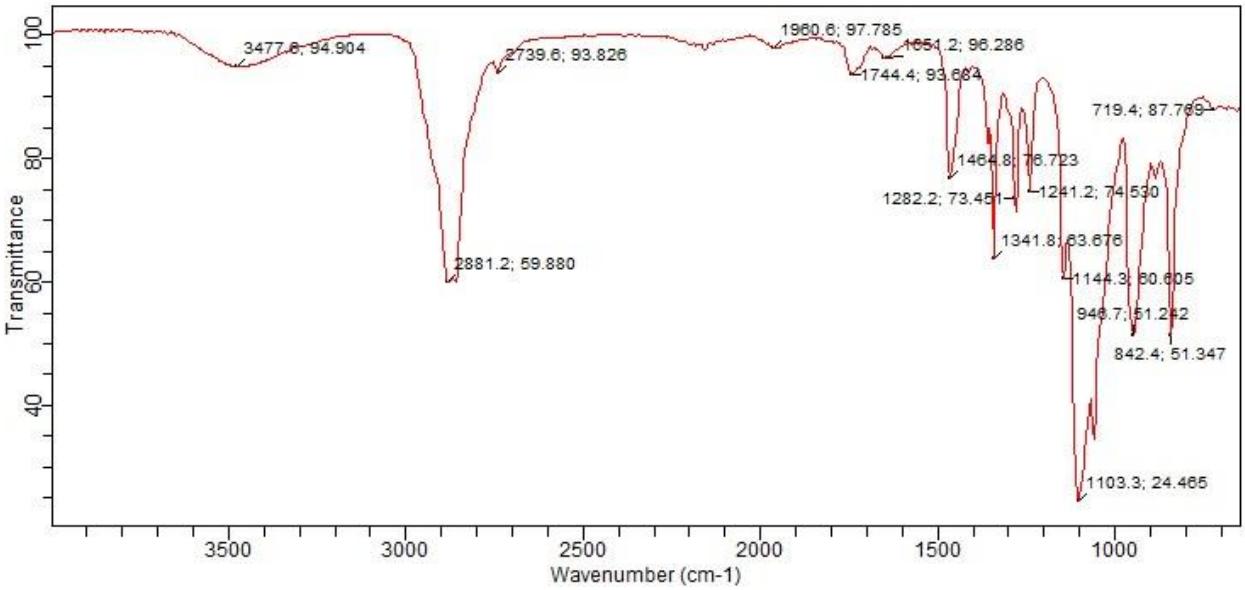

Figure 2. Microcrystalline WC (15wt%) particles reinforced polyester matrix composite FTIR spectroscopy.

Figure 2 shows the FTIR spectrum of a 15wt% wood charcoal particles reinforced polyester matrix composite. Strong stretching in O-H groups resulted in a high transmittance of 94.904 in the FTIR spectra for the band at 3477.6cm-1. This H-bonded O-H stretch is generally found in the frequency region of 3500 – 3200cm^{-1} on the infrared correlation chart for alcohols and phenols (Burns, 2016). This band for unsaturated polyester has been observed by other researchers at 3448cm^{-1} (Cecen et al., 2008). The C-H bond could be responsible for the medium intensity stretching measured at 2881.2cm^{-1} with a transmittance of 59.880 (this is usually found in both alkanes and aldehydes) (Prakash & Viswanthan, 2019). The high transmittance of 93.684 at 1744.4 cm^{-1} could be due to strong C=O stretching from unsaturated ketones and aldehydes. Researchers elsewhere found the same intense stretching vibration in unreinforced polyester at 1728cm^{-1} (Cecen et al., 2008). The band at 1654.2cm^{-1} could be linked to a medium bend of N-H functional groups present in amines. A moderate intensity CH_3 asymmetrical bending of C-H groups (Prakash & Viswanthan, 2019) and moderate stretching of the C-C bond observed in aromatics may be matched to the band at 1464.8cm^{-1} with a transmittance of 76.723. The significant stretching vibration of C-O is connected to the FTIR spectrum range 1282.2cm^{-1} (normally observed for carboxylic acids, alcohols, ethers and esters functional groups). The C-N stretching vibration is matched to the medium transmittance IR band at 1241cm^{-1}. C-O stretching seen at 1282.2cm^{-1} is considered to be the cause of weak molecular interactions between CH2 groups and reinforcements (Cecen et al., 2008). The medium stretching vibrations of C-N seen in aliphatic amine functional groups could be connected to the FTIR band range 1144.3 – 1103.3cm^{-1}. FTIR band 1341.8cm-1 revealed medium symmetrical stretching of N=O observed in nitro compounds at a transmittance of 63.676. The medium intensity stretching vibration of the C-Cl bond found in alkyl halides is usually fixed at 850 – 550cm^{-1} range of frequency on the infrared correlation chart (Burns, 2016), but this medium intensity stretching vibration of the C-Cl bond was seen at 842.4cm^{-1} with a transmittance of 51.347 in the current investigation. The medium IR band at 946.7cm^{-1} has been linked to O-H bending vibrations, which are common in carboxylic acids. The significant IR transmittance band at 719.4cm^{-1} could be due to C=O stretching vibrations present in saturated and unsaturated esters.

3.3. SEM Morphology and Energy Dispersive x-ray Spectroscopy (EDS) Examination

The elemental contents of the composites were disclosed by the EDS mapping and spectra provided in Table 2 and Figure 3. Ca, K, C, Si, Ag, Cl, P, S, and Al were the major constituents in the composites, with traces of Mg, Na, Fe, and Ti in the 15% wood charcoal composite. The quantities of the various chemical ingredients in the composites was controlled by the filler. Figure 3 also shows a SEM micrograph of a 15 wt% wood charcoal reinforced polyester composite. On the micrographs, there are fewer regions where wood charcoal particles agglomerates can be seen. Agglomerations of reinforcement particles in certain zones of composite materials have been attributed to the generation and concentration of stress in these zones, which could act as fracture initiation sites (Hossain, 2012). There is substantial interfacial adhesion, as observed in the micrograph. The porous structure of WC and presence of volatile elements could explain the improved filler-polyester matrix interfacial bonding seen in the SEM image (Edoziuno et al., 2020; S. Li et al., 2015; S. Li & Li, 2014; X. Li et al., 2013; Mochane et al., 2019). Moreover, the filler phase has a homogeneous distribution inside the matrix phase.

Table 2. EDS elements table of a polyester matrix composite reinforced with 15 wt% wood charcoal particles.

Element Symbol	Weight Concentration (%)
C	77.49
Ca	5.82
Ag	4.39
K	2.67
Si	2.65
Cl	1.82
S	1.59
P	1.55
Al	0.93
Mg	0.59
Na	0.50
Fe	0.00
Ti	0.00

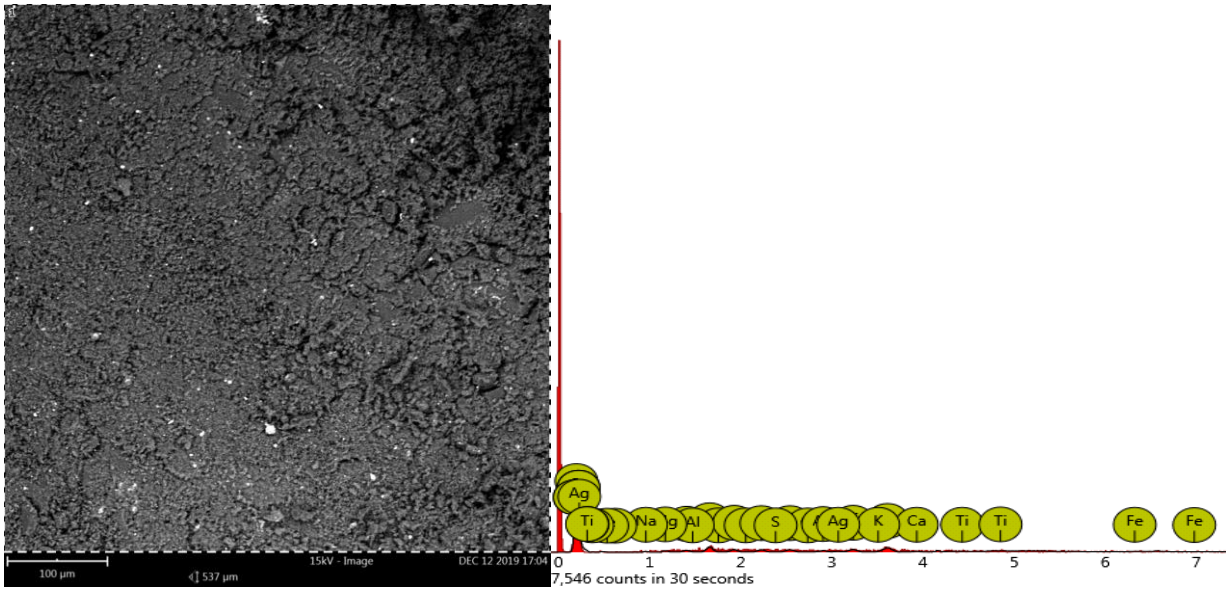

Figure 3. SEM micrograph and EDS spectra of a microcrystalline wood charcoal reinforced polyester matrix composite containing 15% microcrystalline wood charcoal.

4. CONCLUSION

The key chemical components in the polyester matrix composites reinforced with microcrystalline wood charcoal, as determined by various characterization tools and methodologies, are iron, copper, zinc, and calcium, while the predominant oxides in the wood charcoal are CaO, Fe_2O_3, CuO, and ZnO, respectively. Owing to the homogenous distribution of filler particles in the polyester matrix, the porous nature, and the content of volatile compounds described in wood charcoal, SEM micrographs revealed significant filler-matrix interfacial adhesion produced with more wood charcoal. Slight shifts in the assigned peaks for unsaturated polyester were seen in the infrared radiation spectrum acquired in the 600 – 4000cm^{-1} wave number range, which was induced by interactions between the wood charcoal particles and the functional chemical species

in polyester molecules.

Availability of data and materials

All data generated or analysed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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