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Fourier transform infrared spectroscopy analysis of bio-based composite utilizing citrus waste: a comparative study

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Abstract

Citrus fruits as typical agricultural processing wastes were used as sources and raw materials to extract the highly value-added compounds such as pectin, cellulose, lignin and phenols. These chemical compounds were investigated and used to develop novel bio-based materials specifically for plastic and packaging applications in a vast field industry. The properties, bonding and chemical composition of the biocomposites from various studies were comparatively investigated by Fourier transform infrared spectroscopy (FTIR). Results showed that hydrogen bonding, carbonyl groups, alkyl and aromatic ring of lignin and several minor chemical compounds present in the citrus wastes composite illustrate the unique properties, ability and potential materials as guidance in producing the desired products.

1. Introduction

Bio-based products are one of the best and most challenging alternatives replacing the conventional petroleum and crude oil-based products in markets nowadays which harmfully affect human and wild lives (Bassani *et al.,* 2019). Residues from various industries such as food processing industries, juicing and restaurants portrayed adverse effects and harmful consequences specifically to the environment. Citrus wastes (CW) originating from citrus fruits are an example of the aforementioned residues where systematic and effective valorization of these agro-industrial wastes management is requisite. CWs mostly produced by the citrus fruit processing industry where half of their citrus fruit weight is converted into waste (Gurram *et al.,* 2018). An abundant amount of highly valuable chemical compounds is confined in CWs, including essential oils, limonene, phenols and sugars; monosaccharides, disaccharides and polysaccharides. The majority of polysaccharides (cellulose, hemicellulose and pectin) are components of CW peels. Monosaccharides (sucrose, glucose and fructose) and disaccharides occupy the pulp.

Special properties exhibited by these compounds display the characteristics needed for product invention and innovation. For example, essential oils and orange peel powder (OPP) are used for developing antimicrobial films and coatings commonly in food packaging (Mckay *et al.,* 2021). The natural role of pectin and cellulose in providing mechanical strength to the cell wall of plants encouraged and suggested these compounds to be employed as a matrix in biocomposite materials. Citrus wastes are collected and redeveloped as a new source of raw material, source of energy and being employed in the vast field of applications including food packaging (Gurram *et al.,* 2018) and security, such as poultry rations (Chaudry *et al.,* 2004), development of bio-based products such as paper (Yousset *et al.,* 2019), commercial plastics (Baron *et al.,* 2017) and medical tools.

Infra-red (IR) spectra associated with the study of matter and electromagnetic fields' interaction in the IR region. EM waves are coupled with the molecular vibrations in this spectral region. The molecules absorb the IR radiation and are excited to a higher vibrational state. After being absorbed, the IR frequency would interact with the molecules at a certain frequency. Thus, IR spectroscopy is a very powerful method that provides fingerprint information on the sample's chemical composition and both qualitative as well as quantitative analysis can be carried out. FTIR works based on the Fourier Transform principle as shown in Figure 1. It is one of the techniques found to be the most analytical technique type available in the laboratories. FTIR spectroscopy experimentally determined the interferogram. The spectrum we see on the computer is

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plotted against the corresponding wavenumber against transmittance values. The displayed spectrum or infrared spectroscopy results in qualitative analysis (identification). In addition, the size of the peak in the spectrum directly indicates the amount of material present. Infrared is an excellent tool for quantitative analysis, particularly with modern software nowadays (Ramaiah *et al.,* 2017).

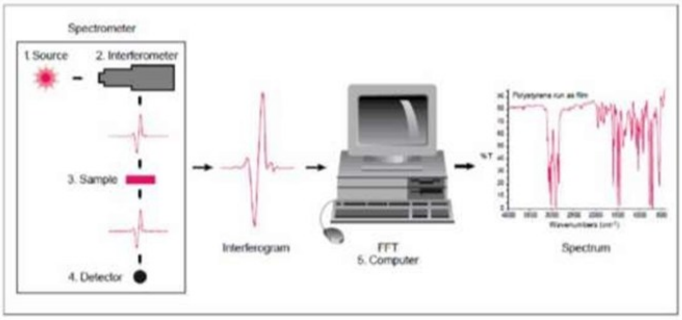

Figure 1. Illustrate the working principle of Fourier transform infrared (FTIR) spectroscopy.

2. Materials and methods

The orange peels (OP) were brought and collected from supermarkets and also from the daily main meal served at home. The citrus peels were washed and soaked overnight in tap water to remove soluble sugar, unwanted particles and adhering dirt as shown in Figure 2. Cracks appeared on the surface of OP film with the presence of soluble sugar, thus removing them is necessary (Bassani *et al.,* 2019). Then, the OPs were cut into small pieces and dried using an oven at 60-80°C for 24 hrs. The moisture of OP should be approximately less than 10% of the initial wet weight. Too dry will make the OPs brittle and difficult to grind. The powder form of OPs was achieved by grinding, blending and sieving till the fine powder was formed. Smaller the size results in more mechanical properties enhancement. The ratio of epoxy resin and hardener is 3:1 which were then mixed with 1.0g of ferrite magnetic powders. The biofilms were produced with different compositions of OPs powder; 5, 10, 15 and 20 wt%. The mixtures were shaped using the casting method and left dried at the surrounding temperature overnight. The functional groups present in the samples were analyzed by FTIR spectrometer (Perkin Elmer FT-IR, C114769) at room temperature. The spectral range was from 4000-400 cm^{-1} with a resolution of 4 cm^{-1} (Anbusagar *et al.,* 2018).

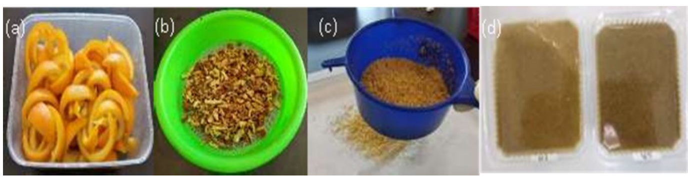

Figure 2. The process of (a) washing and soaking, (b) drying, (c) blend and sieving, and (d) casting for orange peels biofilm production.

3. Results and discussion

3.1 Orange peels and magnetic powder filler as commercial plastic

The infrared analysis was carried out using Fourier Transform Infrared Spectroscopy (FTIR) model DVIA-T56 over the range 500-4000 cm^{-1}. Spectroscopic analysis of FTIR gave valuable information regarding the functional groups' presence in the orange peels bioplastic, ferrite powder and the composites as well as the behavior when the concentration of orange peels is varied. Figure 2 shows the FTIR spectra of the orange peel bioplastic. It can be seen that bioplastic consists 5% OP concentration has the lowest hydrogen bonding within 3100 cm^{-1} to 3600 cm^{-1}, while the O-H bonding stretches greatly for 10%, 15% and 20% respectively (Ricardo *et al.,* 2006; Fan *et al.,* 2006). This bonding indicates the stretching of cellulose type I confined in the citrus fruit (Fan *et al.,* 2006). There is a medium absorption intensity of alkenes around 3020 -3100 cm^{-1}. These kinds of infrared absorptions are caused by the vibration of the ≡C-H asymmetric stretch. There is also vibration at the wavenumber of 2850-2960 cm^{-1} corresponding to the presence of the alkanes, C-H. Narrow peaks of absorption occur between 1600-1580 cm^{-1} signifying the symmetric stretching of C -C=C for an aromatic ring of lignin (Yousset *et al.,* 2019).

3.2 Fourier transformed infrared analysis of citrus wastes as biocomposite materials: a comparative study

A high-purity and robust cellulose, Bacterial cellulose (BC) is utilized in medicine, consumer goods and industrial practices. It has been commercialized in paper additives, dressing of the wound, filtration membranes and diet food. It is noticeable that currently, high-sugar fruits such as orange peel, pineapple juice peel and grapes have been used as a medium to produce BC. A study of nano bacterial cellulose production from agricultural wastes, presents the comparison of FTIR spectra of BC in a different medium, citrus peel and pomace enzymolysis (CPPE) medium (black curve) and Hestrin-Schramm (HS) medium (red curve) respectively as shown in Figure 3. There are several important absorption characteristic peaks observed from the FTIR spectrum of two BC varieties. A broad peak at 3353 cm^{-1} indicates the O-H stretching of cellulose type I while asymmetric stretching of -CH_2CH, causes the IR absorption at 2898 cm^{-1}. At wavenumber 1163 cm^{-1} and a broad peak of 1066 cm^{-1}, represents the asymmetric stretching of C-O at the ring and C-O stretching respectively. It can be seen that there is a noticeably different wavenumber around 1650 cm^{-1} in the results illustrated by the absorbed water H-O-H bending motion

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which specifies that C-O shows only a slight difference between the BC produced by CPPE and HC media. From the results, it can be confirmed that nearly unanimous chemical groups had in the two varieties of BC (Fan *et al.,* 2006). Youssef *et al.* (2019), conducted research for the production of wood plastic composites (WPC) utilizing lignocellulosic fibers from citrus trees. The fibers were modified with *Aspergillus flavus* (EGYPTA5) enzymes. Two types of WPC are produced; the non- modified and the modified, where low-density polyethylene (LDPE) is used with lignocellulosic fibers by melt blending Brabender method at 170°C into different ratios (5, 10 and 20 wt%) to produce the WPC. The presence of chemical structures in modified and unmodified WPC analyzed by FTIR and illustrated in Figure 4. The stretching of the carbonyl group at 1700 and 1600 cm^{-1} in the unmodified lignocellulose correspond to the ester and acetyl groups in the lignin and hemicelluloses. On the other hand, this peak disappears in the modified lignocellulosic as an indication of hemicellulose removal effectiveness by the fungal enzyme. The 1700 cm^{-1} peaks indicate the stretching vibration of the C-O hemicellulose acetyl group or ester linkage among ferulic carboxylic group and lignin p-coumaric acids which is obtained in untreated fibers and becomes faint for treated fibers.

Likewise, 1600 cm^{-1} absorption peak is only present at unmodified Lignocellulosic, that associated with C-C stretching vibration of the lignin aromatic ring. The absence of this peak is also due to the removal action of hemicellulose and lignin by fungal treatment. Absorbance peak regions of 1641-1649 cm^{-1} of modified fibers are caused by O-H bending of absorbed water.

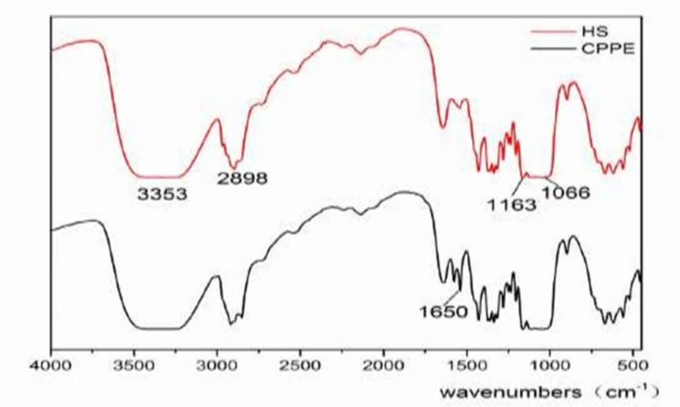

Figure 4. FTIR spectra of bacterial cellulose obtained by different mediums; citrus peel and pomace enzymolysis (CPPE) (black curve) and Hestrin-Schramm (HS) (red curve). Source: Fan *et al*. (2006).

Another research by Ricardo *et al.* (2017) for the production of a film based on blends of pectin and chitosan. Both compounds were extracted from waste products, where chitosan was obtained from blue crab (*Callinectes sapidus*) waste and orange peel waste (*Citrus sinensis* Osbeck) for pectin. The study proves

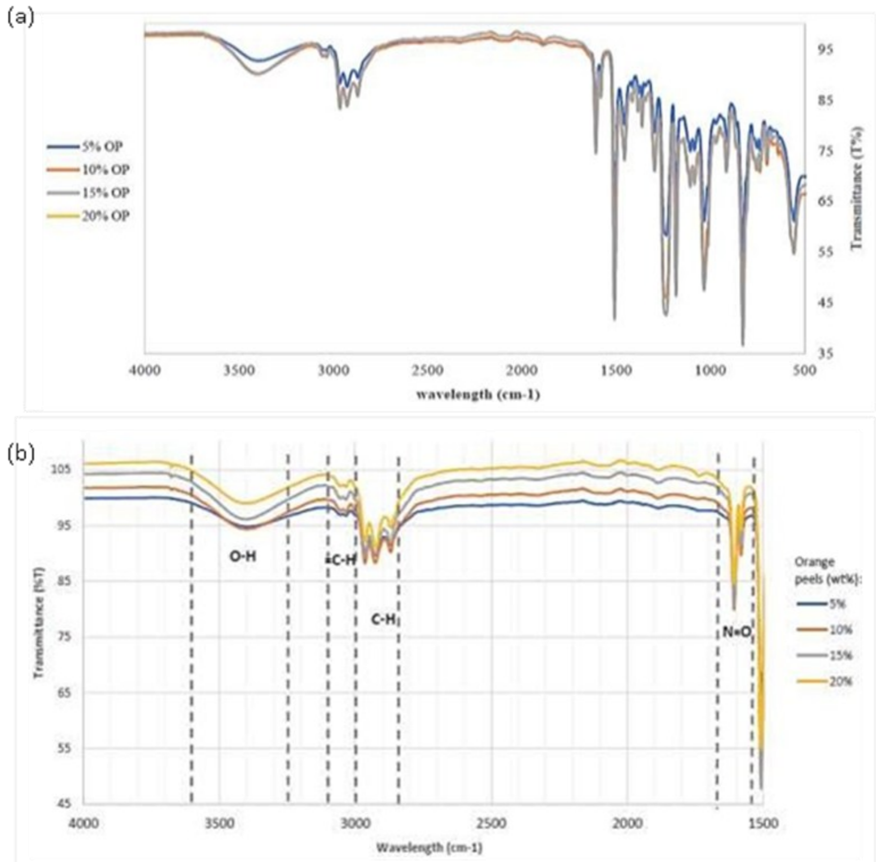

Figure 3. FTIR spectrum (a) combined graph and (b) stacked line graph of orange peels bioplastic with various concentration reinforced with 1.0 g ferrite magnetic powder filler.

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and suggests that agro-industrial waste of chitosan and pectin is a potential matrix to produce biodegradable films for future food applications and industries. In Figure 5, the pectin FTIR spectrum showed the presence of free carbonyl groups at 1741 cm^{-1} and esterified carbonyl groups at 1632 cm^{-1}. The region of polysaccharides is illustrated in the 1200-800 cm^{-1} range. 3300 cm^{-1} band corresponds to free or substituted OH groups and galacturonic acid residues compound at 1018 cm^{-1}. In addition, it is observed that the wavenumber of the 1632 cm^{-1} peak is caused by the vibration of the carbonyl group of carboxylate ion (COO -) asymmetric stretching.

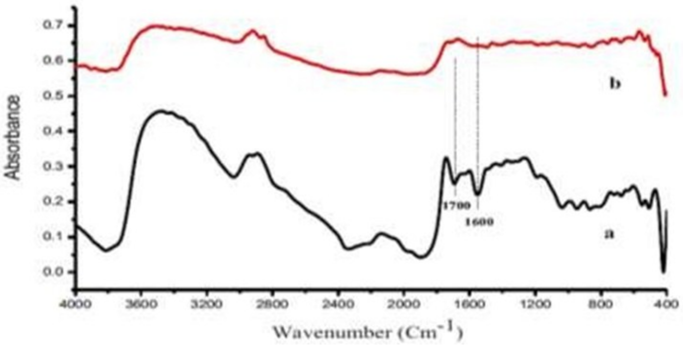

Figure 5. Spectrum analysis of FTIR (a) unmodified lignocellulose and (b) modified lignocellulosic fibers. Source: Youssef *et al.* (2019).

Citrus pomace is derived from juice processing industrial and essential oils confined highly valuable chemical compounds including pectin, cellulose, hemicellulose and simple sugars. To develop novel biocomposite-based materials, pectin extraction was reinforced with various amounts of lignocellulose fractions which were both extracted from citrus wastes, according to a "zero waste" circular economy approach. The upgraded pectin after 6 hrs to 3% (*v/v*) recovery of HAc, purified pectin and commercial citrus pectin are structurally characterized by FTIR to be used as a mulching system for crop protection as shown in Figure 6. According to Zannini *et al.* (2021), it is possible to observe the strong and wide elongation vibration attributed by the O-H at peak 3364 cm^{-1} and C-H elongation vibrations of CH_2 and CH_3 groups in the pectin induced the 2936 cm^{-1} peak. 1731 cm^{-1} and 1608 cm^{-1} IR absorption were due to the C=O stretch vibration of methyl esterification carbonyl and to the free carbonyl of asymmetric stretch vibration of C=O, accordingly. 1143 cm^{-1} and 1048 cm^{-1} absorption bands correspond to the lateral groups C-OH stretching vibrations and to the glycosidic bond C-O-C vibration as shown in Figure 7.

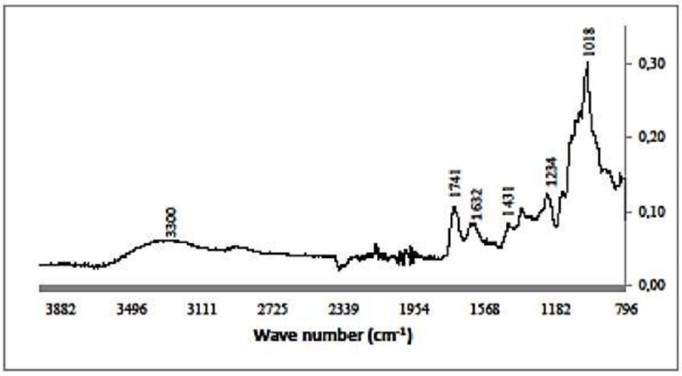

Figure 6. FTIR spectra of pectin extracted from *Citrus sinensis* Osbeck for production of bioplastic film blends with chitosan. Source: Ricardo *et al*. (2017).

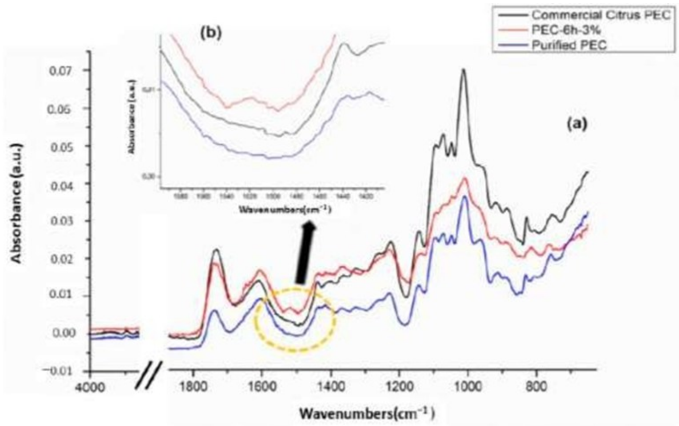

Figure 7. FTIR-ATR spectrum of (a) all samples of pectin and (b) presence of bioactive molecules peak Source: Domenico *et al*. (2021).

4. Conclusion

From the studies, it can be concluded that citrus waste from industries is a feasible source of raw materials, energy sources as well as a filler, which has excellent potential to be exploited in packaging films and bio-composite materials that are renewable, biodegradable and also biocompatible. The spectrum analysis of FTIR assists in determining the structural and composition of the chemical groups present during the binding of the bio-composite which reveals the binding of the O-H group, alkyl groups, lignin aromatic rings and carbonyl group in the pectin. Research and comparative studies reveal a novel approach to utilizing the wastes from citrus juicing processing for bio-based commercial plastic and packaging and other sustainable products, simultaneously minimizing the amount of conventional plastic and used packaging by half to realize a zero-waste environment.

Conflict of interest

The authors declare no conflict of interest.

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