Research Article

Elemental and Infrared Characterization of Contaminants in Second-Hand Cotton Garments From Flea Markets In Valencia City, Bukidnon, Philippines

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Abstract
The use of Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) characterizations have been indispensable techniques in distinguishing purity of the samples. These techniques give spectra that will be used to analyze the composition, morphology, purity, among others, of the material. One of its interesting applications is to assess elemental and chemical contaminations on second hand clothing. In this study, second hand (Ukay-Ukay) cotton garments from selected flea market sites in Valencia City, Bukidnon, Philippines were examined quantitatively for microbial and chemical contaminations by using FTIR, SEM, and EDX. The FTIR results obtained in both sites showed broad peaks at ~3336 cm⁻¹ attributed to OH functional group, and absorption peaks at 2901.30 cm⁻¹ associated to C-H bond, 1159.70 cm⁻¹, 1107.44 cm⁻¹ and 1053.82 cm⁻¹ attributed to the stretches of CO bond. All of them were characteristics of cotton material. We observed degradation of the cotton material on both sites evident in the decreasing intensity of OH stretching (at peaks around ~3334 cm⁻¹ [site A] and ~3332 cm⁻¹ [site B]) and C-O stretching (around ~1500-1700 cm⁻¹). These were due to the presence of microorganisms such as fungi (e.g. Aspergillus species). The degradation was also observed in the SEM results. Furthermore, peaks related to carboxylate contaminations were observed in both sites around ~1600 – 1800 cm⁻¹ that may be caused by the exposure of the cotton garments in hydrochloric acid (HCl). In general, the characterization results on both sites indicated traces of microorganisms and that the second-hand cotton clothes were contaminated by hazardous chemicals.

Keywords: infrared properties, second hand garments, Ukay-Ukay, chemical contaminants, cotton degradation

Karakterisasi Elemen dan Infrared dari Kontaminan pada Garmen Katun Bekas dari Pasar Loak di Kota Valencia, Bukidnon, Filipina

Abstrak
Penggunaan karakterisasi Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), dan energy dispersive X-ray (EDX) telah menjadi teknik yang sangat diperlukan...
I. INTRODUCTION

Clothing is a feature of nearly all human societies, aside to the fact that clothing is one of the basic human needs and substantially serves as protection from the hazardous elements. Its primary function is to improve the comfort of the wearer and enhances safety during hazardous activities. Today, it has become one of the most fascinating and expensive items (branded garments) in the fashion industry. This leads consumers to divert their interest into second-hand clothes.

In the Philippines, the common term of second-hand garment is called “Ukay-Ukay or Wag-Wag”. These garments were imported from various countries. According to Philippines Journal of Development [1], one of the core concepts in the market demand analysis was that of consumer surplus. However, clothing may become a source for growth of microorganisms [2,3] such as pathogenic or odor-generating bacteria and fungi that whenever in contact with human body bid an ideal environment for microbial growth since it provides oxygen, moisture and warmth [4]. Pathogens, bacteria (scabies, pediculosis, among others), fungal and nosocomial infections can be a possible disease that could be found and transferred through the clothes or even hospital uniforms usage [5-7].

There were studies that discussed contaminations in some clothes by chemical and biotic factors such as the study of Y. M.
Muthiani and colleagues [7]. They reported a variety of potential skin pathogens found in unwashed second hand under garments such as bras and panties, socks and towels. Interestingly, there was a study pointing out that imported clothes could be one source of carrying diseases and growing toxic chemicals and infectious pathogens as well as threats of biological and chemical attacks from terrorists to other country [8]. Recently, the presence of microbial flora in second hand garments (Ukay-Ukay) from flea markets in Valencia City, Bukidnon, Philippines was reported [9]. This leads to the idea that conducting elemental and chemical investigations in second-hand clothes is an opportunity to scrutinize if there can be traces on the spectra of any certain microorganism and hazardous chemicals rather than protection from wearing it.

Hence, in this research, the elemental and chemical characteristics of second-hand cotton garments bought from the selected flea markets in Valencia City, Bukidnon, Philippines was investigated for possible traces of microorganisms and hazardous chemicals using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. Moreover, there is no existing research conducted in the Philippines on the chemical contaminations of second hand garments by using these techniques especially in Valencia City, Bukidnon, Philippines.

II. RESEARCH METHOD
Sample Preparation

Based on the site observations and interviews, two sampling sites referred to this study as sites A and B were identified as the main source (seller) of second-hand cotton clothes in Valencia City, Bukidnon, Philippines.

The samples were classified as to the consumer demand usage such as shirt/blouses but limited to cotton fabric for sampling control purposes.

![Schematic Flow Chart of Sample Collection, Preparation, and Characterization](image)

Figure 1. Schematic Flow Chart of Sample Collection, Preparation, and Characterization

The second-hand cotton fabrics bought from selected sites in Valencia City, Bukidnon, were placed to sterile polyethylene bag with desiccant silica gel. Portion of the cloth was cut into 0.01 m x 0.01 m dimension for FTIR, SEM and EDX characterizations.

FTIR Characterization

The 0.01 m x 0.01 m dimension of cloth was being coated with potassium bromide (KBr) to make the sample transparent to infrared light and was scanned at wavenumber range 4000 – 500 cm⁻¹ using Perkin Elmer Spectrum 100 FTIR Spectrometer for IR analysis and identification. The raw data were plotted using SciLab software [10]. Then the absorption peaks were identified through comparison with standard reference materials.

SEM-EDX Characterizations

The 0.01 m x 0.01 m dimension of cloth samples was coated with Platinum to reduce surface charging. Then, surface morphology of the second-hand clothes samples was obtained using scanning electron microscope (JEOL Model: JSM-6510) at an accelerating voltage of 20 kV with 0.3 mm bar magnification. On the other hand, EDX spectra were obtained during SEM.
characterization (SEM coupled with EDX). Atomic percentage of each element present was recorded to determine the major elements that composes the samples.

III. RESULTS AND DISCUSSION

Table 1 shows the elemental compositions of the samples in sites A and B. Site A sample was observed to contain carbon, oxygen and chlorine. We note that both samples (sites A and B) contain chlorine. Pure cotton material does not contain chlorine. This may suggest that both samples were exposed to chlorine before display in every site.

Furthermore, it was remarkable to observe elements such as calcium, sodium and aluminum in the sample found in site B. Calcium, sodium and aluminum elements were derivatives of chemicals introduced to the second-hand cotton sample.

Table 1. Elemental composition of the second-hand cotton sample with atomic percentage.

<table>
<thead>
<tr>
<th>Element</th>
<th>Site A (Atomic %)</th>
<th>Site B (Atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>59.63</td>
<td>61.44</td>
</tr>
<tr>
<td>Oxygen</td>
<td>40.28</td>
<td>38.08</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.00</td>
<td>0.10</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.00</td>
<td>0.22</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.00</td>
<td>0.07</td>
</tr>
</tbody>
</table>

FTIR and SEM Analyses

Figure 2 shows the superimposed FTIR spectra of the second-hand cotton samples (obtained in sites A and B). The spectra show broad bands, characteristic of cellulose (main component of cotton fiber), at ~3334 cm⁻¹ (site A sample) and ~3332 cm⁻¹ (site B sample) ascribed to OH functional stretching [2,11,13,15,17].

Moreover, there are absorption peaks at ~2899 cm⁻¹ (site A sample) and ~2917 cm⁻¹ (site B sample) associated to C-H bond stretching, which may indicate the presence of
waxes and oils [12,14]. The C-H bond stretching peaks decreased their intensity as you go from sites B to A indicating that the sample obtained in site A has degraded more than in site B. The hydrogen bonds, methyl and methylene of cellulose had some fraction which could make the organisms attack the cellulose easily [13,17-20]. This was reasonable since microorganisms preferred environment with hydrogen-bonded water molecules. Likewise, characteristic peaks of cotton were observed at ~1159 cm\(^{-1}\), ~1108 cm\(^{-1}\), ~1054 cm\(^{-1}\) (site A sample) and ~1159 cm\(^{-1}\), ~1107 cm\(^{-1}\), ~1053 cm\(^{-1}\) (site B sample), which were attributed to glucose ring vibrations, C-O stretching modes, etc. [15].

The former peaks represent the antisymmetric stretching of the C-O-C groups in the cellulose [13,15]. Another absorption peak for cellulose was observed at ~1427.71 cm\(^{-1}\) associated to CH\(_2\) bending [15]. We noticed that the bands around the range ~1500-1700 cm\(^{-1}\) for C-O stretching decreased expressively which may entail degradation like the trend of FTIR data reported by Li, Frey, and Browning [13]. This degradation may be associated to the presence of microorganisms such as fungi (e.g. *Aspergillus* species) [16]. This result complements with Samaniego and Elumba [9] as they recovered and identified several microorganisms found in the second-hand garments in the flea markets of Valencia City, Bukidnon, Philippines.

Indeed, Figures 3 and 4 showed that the cotton clothes started to degrade. The fibers were disassembled, and the knitting pattern became irregular.

On the other hand, there were peaks related to the presence of carboxylate groups (~1600-1800 cm\(^{-1}\)) which suggest that the samples were exposed to HCl [11]. The presence of chlorine was observed in the EDX analysis as reflected in Table 1. These carboxylates were impurities of the cotton fabric [11] which can be removed normally through washing.

Other information such as peaks around ~1314 cm\(^{-1}\), ~1315 cm\(^{-1}\) (sites A and B samples) associated to CH\(_2\) wagging [15] and ~665 cm\(^{-1}\) (site A sample), 663 cm\(^{-1}\) (site B sample) which were related to the vibration modes of cellulose [17] were observed. Likewise, we observed C-H deformation peaks around (~900 - 800 cm\(^{-1}\)) in both sample sites [15]. Finally, the bands around the finger print region (~800 - 600 cm\(^{-1}\)) were difficult to interpret but mostly belong to cotton cellulose as reported by Sugiyama, Person, and Chanzy. [17].
IV. CONCLUSION

In this study, we have shown that the EDX and FTIR results conform to the elemental and chemical compositions of the cotton fabric. However, EDX showed elemental contaminants in the samples found in both sites A and B. Site B was found to have the most numbered contaminants. The elemental contaminants observed were chlorine, aluminum, calcium and sodium. Furthermore, FTIR results showed vibrations of chemical compounds associated to the presence of contaminants such as carboxylate.

Moreover, the samples (Ukay-Ukay) of cotton fabric started to degrade as shown in SEM photomicrographs in (Figures 3 and 4). The degradation of the cotton material was also evident in the decreasing intensity of OH stretching (at peaks around ~3334 cm⁻¹ [site A sample], ~3332 cm⁻¹ [site B sample]) and C-O stretching (around ~1500-1700 cm⁻¹) on both sites found in Figure 2. Finally, the degradation of the cotton material suggested the presence of microorganisms such as fungi (e.g. Aspergillus species).

Seeing these microorganisms on the surface of the cotton clothes at higher magnification via SEM will be a nice future direction of research.

ACKNOWLEDGMENT

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[9] Samaniego LG and Elumba E. Microbial Flora in Ukay-Ukay from Flea Markets in


