Determination of chemicals released from single use low density polyethylene plastic bags

Ei Ei HTWAY 1, Aye Thida HTUN 1, Thiri HLAING 1, Moh Moh LWIN 1, Hla Myoe MIN 2
1 Department of Medical Research (Pyin Oo Lwin Branch), Myanmar
2 University of Mandalay, Myanmar

E-mail: eieihtwaydmr@gmail.com

Abstract. The use of plastics has increased manifold, owing to their inexpensive, multipurpose, durable and lightweight nature. Plastics are made with various types of polymer, including Low Density Polyethylene (LDPE). In Myanmar, many foods are packaged in single use LDPE plastics including fresh meat, vegetables, fast foods, and even some hot foods in daily life. Therefore the present study was aimed to determine the chemicals released from single use LDPE plastic bags that were used in direct contact with hot foods. Fourier Transform Infra-Red (FTIR) spectroscopy analysis was done for confirmation of LDPE. Extraction of chemicals from single use plastic bags was carried out by reflux extraction method by using four types of solvents (chloroform, ethanol, distilled water and olive oil). The individual chemicals released from the sample were determined by Gas Chromatography- Mass Spectrometry (GC-MS) with National Institute of Standard and Technology (NIST) library. GC-MS results of different extracts were hexadecanoic acid octyl ester (26.09%), octadecanoic acid octyl ester (19.96%), tetracosane (13.36%) and 9-octadecanoic acid methyl ester (9.28%) from distilled water extract; 3-methoxy 2,2-dimethyloxirane (84.26%), 2,3-dihydro-1,4-dioxin (3.77%), 1-ethoxy pantane (2.85%) and tetracosane (2.65%) from ethanolic extract; toluene (69.30%), ethyl benzene (18.11%), 1,1-dipropoxypropane (4.02%) and dipropoxy methane (1.56%) from chloroform extract; and supraene (76.81%), nonanal (3.09%), 2-decenal (2.97%), 2-undecenal (3.05%) and toluene (1.35%) from olive oil extract respectively. According to the Wavelength Dispersive X-ray Fluorescence (WDXRF) analysis of single use plastic bag, the different concentrations of elements were found to be titanium (0.0587 %), chlorine (0.0093 %) and strontium (0.0026 %) and so on. The present study revealed that single use LDPE plastic bags contained some chemicals that are toxic to human beings such as toluene, ethyl benzene, methyl oxirane, supraene and some type of aldehyde, and even carcinogenic substance like dioxin. Therefore it is necessary to limit the use of harmful additives and packaging of hot foods in single use LDPE plastic bags.

1. Introduction
The use of plastics has increased manifold, owing to their inexpensive, multipurpose, durable and lightweight nature. Plastics are made with various types of polymer, including Low Density Polyethylene (LDPE) [1]. But plastic can contain smaller chemical molecules, plastic additives that are free to migrate into food during contact time and thereby cause health problems [2]. Some additives used in plastic are even carcinogenic or tumorigenic [3]. And then the recycling of plastic materials may increase the levels of potentially hazardous chemicals in the plastic packaging [4].
Diffusion of chemical substances from polymers is a very complex process, and is dependent on several parameters, such as concentration of substances in packaging film and food, nature of the foods, temperature, and the time period over which duration of contact occurs [5]. Actually, carrying of retail foods by single use plastic bag is beneficial for user because it can protect the carried foodstuff from spoilage by external agents such as dust, micro-organisms, and then provide easily accessible by consumers. Food contamination refers the occurrence of toxic chemicals and microbial pathogens which could produce negative health implications to the humans after prolonged exposure at low levels [6]. Then, the migration of chemicals from single use plastic bags to food may also have a negative impact on the quality and safety of food.

In fact, no food contact material is completely inert and so it is possible for their chemical constituents to ‘migrate’ into the packaged food. Metals, glass, ceramics, plastics, rubber and paper can release minute amounts of their chemical constituents when they touch certain types of foods [7]. In Myanmar, many foods and food related substances are packaged by using single use LDPE plastics bags including fresh meat, vegetables, fast foods, and even some hot foods in daily life. Although the use of LDPE plastic bags was being moved to ban in Myanmar to protect the environment [8], the LDPE plastic bags were being used as primary and secondary packaging for food.

Fourier Transform Infrared Spectrophotometer (FTIR) is a high resolution analytical technique to identify the chemical constituents [9]. Gas Chromatography–Mass Spectrometry (GC-MS) is a hyphenated analytical technique that combines the separation properties of gas-liquid chromatography with the detection feature of mass spectrometry to identify different substances within a test ample. Congruence of mass spectra is convincing evidence for identification and is often even admissible in court [10].

There is no scientific research concerning about the chemicals released from single use LDPE plastics in Myanmar. Therefore, the present study was aimed to determine the chemicals released from single use LDPE plastic bags that were used in direct contact with hot foods in Myanmar.

2. Materials and Methods

2.1. Sample collection
Single use plastic bags (6 x 11 inches, white color) were collected from the market of Pyin Oo Lwin. The collection based on most frequently used sizes by hot food distributor such as tea shops, Myanmar noodles with hot soup (Mont-Hin-Khar), fried cakes and other Myanmar fried foods.

2.2. Identification of type of polymer
Fourier Transform Infra-Red (FTIR) spectroscopy analysis was done for identification of type of polymer. In this method, single use plastic bags were cut into small pieces and covered into KBr sample holder and then analyzed in the mid IR region (400–4000 cm⁻¹). The spectra obtained were identified by specialized data software (Raman of basic monomers and polymers).

2.3. Extraction of chemical compounds from the samples
Extraction of chemicals from LDPE plastic bags was carried out by reflux extraction method using four types of solvents (distilled water, ethanol, chloroform and olive oil) at the reflux temperature for 30 minutes. The extracts were filtered by filter paper (Whatman No.1) and store in the stoppered vial for further analysis.

2.4. Identification of chemical compounds
The individual chemicals from four types of extracts were determined by Gas Chromatography-Mass Spectrometry (QP 2020, Shimadzu, Japan) with National Institute of Standard and Technology (NIST) library. In this analysis, all extracts were measured under specified conditions by using DB-5MS column, the oven temperature was maintained at 50°C for the first 1 minute, and then ramped up at 10°C/min to 270°C where it was held for 22 minutes. The injection port and interface were kept at
260°C. The MS conditions were the ionization mode, electron impact and detection voltage at 1.30 kV [11].

2.5. Analysis of elemental composition
Elemental composition of LDPE polymer was analyzed by Wavelength Dispersive X-ray Fluorescence (WDXRF) at Petro Chemicals Lab, Mandalay. In this analysis, the samples were directly analyzed.

3. Results

3.1. Identification of type of polymer
The FTIR spectrum of the single use plastic bags was shown in Figure (1). All of the absorption maxima of the individual peaks in the samples were consistent with those of library spectrum of LDPE polymer (Figure 2).

![Figure 1. FT-IR Spectrum of single use plastic bag sample.](image)

![Figure 2. Comparison of FT-IR spectrum of plastic bag sample and library spectral data.](image)
3.2. Identification of chemical compounds

Gas Chromatography-Mass Spectrometry (GC-MS) results of different extracts were hexadecanoic acid octyl ester (26.09%), octadecanoic acid octyl ester (19.96%), tetracosane (13.36%), 9-octadecanoic acid methyl ester (9.28%) and others from distilled water extract; 3-methoxy 2,2-dimethyloxirane (84.26%), 2,3-dihydro-1,4-dioxin (3.77%), 1-ethoxy pantane (2.85%), tetracosane (2.65%) and others from ethanolic extract; toluene (69.30%), ethyl benzene (18.11%), 1,1-dipropoxypropane (4.02%), dipropoxy methane (1.56%) and others from chloroform extract; and supraene (76.81%), nonanal (3.09%), 2-decenal (2.97%), 2-undecenal (3.05%), toluene (1.35%) and others from olive oil extract respectively. The GCMS chromatograms of different extracts were shown in Figure (3) to (6) and the identified individual chemicals released from respective extracts were described in Table (1) to (4).

![Figure 3. GC-MS chromatogram of water extract of single use plastic bag sample.](image)

| No | Name of Compound                          | Rt(min) | SI | A%   |
|----|------------------------------------------|---------|----|------|
| 1. | Hexadecane                               | 14.011  | 96 | 3.42 |
| 2. | Heneicosane                              | 17.329  | 96 | 4.72 |
| 3. | Hexadecanoic acid, methyl ester          | 18.942  | 93 | 2.36 |
| 4. | Eicosane                                 | 19.835  | 96 | 5.15 |
| 5. | 9-octadecenoic acid (Z) – methyl ester   | 20.912  | 92 | 9.28 |
| 6. | Tetracosane                              | 21.930  | 96 | 13.36|
| 7. | Octadecanoic acid, octyl ester           | 24.744  | 86 | 26.09|
| 8. | Hexadecanoic acid, octyl ester           | 24.745  | 86 | 19.96|
| 9. | Hexatriacontane                          | 28.755  | 88 | 3.73 |

Rt- Retention time, SI-Similarity Index, A%-Relative Area percent
Figure 4. GC-MS chromatogram of ethanol extract of single use plastic bag sample.

Table 2. Identified compounds from the ethanol extract of single use plastic bag sample.

| No | Name of Compound                        | Rt(min) | SI | A%   |
|----|----------------------------------------|---------|----|------|
| 1. | 3-Methoxy-2,2-dimethyloxirane          | 1.41    | 90 | 84.26|
| 2. | 2-Methoxy butane                       | 1.48    | 91 | 0.70 |
| 3. | 1-Butanol                               | 1.54    | 95 | 0.24 |
| 4. | 2,3- Dihydro-1,4- dioxin               | 1.58    | 91 | 3.77 |
| 5. | 1,1-Diethoxy ethane                    | 1.63    | 94 | 1.76 |
| 6. | 1-Ethoxy-1-methoxy ethane              | 1.69    | 86 | 0.93 |
| 7. | 1-(1-ethoxyethoxy)-propane             | 1.74    | 88 | 0.27 |
| 8. | 1-Ethoxy-pentane                       | 1.80    | 95 | 2.85 |
| 9. | 3-Ethoxy-2-methylacroleine             | 1.92    | 81 | 0.51 |
| 10.| n-Butyl ether                          | 1.95    | 90 | 0.21 |
| 11.| Heptadecane                            | 13.94   | 97 | 0.81 |
| 12.| Heneicosane                            | 17.26   | 97 | 1.03 |
| 13.| Tetracosane                            | 21.87   | 98 | 2.65 |

*Rt- Retention time, SI-Similarity Index, A%-Relative Area percent*
Figure 5. GC-MS chromatogram of chloroform extract of single use plastic bag sample.

Table 3. Identified compounds from chloroform extract of single use plastic bag sample.

| No  | Name of Compound                          | Rt(min) | SI | A%  |
|-----|------------------------------------------|---------|----|-----|
| 1.  | Toluene                                  | 3.127   | 98 | 69.30 |
| 2.  | Tetrachloroethylene                      | 3.798   | 96 | 0.30 |
| 3.  | Propanoic acid, propyl ester             | 3.830   | 97 | 0.19 |
| 4.  | Propane, 1-(1-ethoxy ethoxy)-            | 4.011   | 96 | 0.20 |
| 5.  | Propanoic acid, 2-mercapto-, allyl ester | 4.500   | 81 | 0.66 |
| 6.  | Ethyl benzene                            | 4.865   | 96 | 3.24 |
| 7.  | Dipropoxy methane                        | 4.923   | 95 | 1.56 |
| 8.  | 1,3- dimethyl benzene                    | 5.051   | 98 | 13.87 |
| 9.  | 1,2- dimethyl benzene                    | 5.519   | 98 | 1.00 |
| 10. | 1,1 diethoxy propane                     | 5.664   | 86 | 1.07 |
| 11. | 1,1-[ethylidene bis(oxy)]bis propane     | 5.801   | 97 | 0.87 |
| 12. | 1,1,2,2-tetrachloro ethane               | 6.061   | 98 | 1.81 |
| 13. | Pentachloroethane                        | 7.294   | 95 | 0.79 |
| 14. | 1,1-1,1- dipropoxy propane               | 7.426   | 97 | 4.02 |
| 15. | Hexachloro ethane                        | 9.171   | 93 | 0.25 |
| 16. | 9-octatecenoic acid (Z)- methyl ester    | 25.846  | 98 | 0.85 |

Rt- Retention time, SI-Similarity Index, A%-Relative Area percent
Figure 6. GC-MS chromatogram of oil extract of single use plastic bag sample.

Table 4. Identified compounds from the oil extract of single use plastic bag sample.

| No | Name of Compound                                | Rt(min) | SI  | A%  |
|----|-------------------------------------------------|---------|-----|-----|
| 1. | Toluene                                         | 3.290   | 97  | 1.35|
| 2. | Octane                                          | 3.840   | 95  | 0.95|
| 3. | Heptanal                                        | 5.870   | 95  | 0.41|
| 4. | 2-heptanal (E)                                  | 7.002   | 97  | 0.35|
| 5. | Heptanol                                        | 7.282   | 97  | 0.27|
| 6. | Octanal                                         | 7.932   | 97  | 0.65|
| 7. | 1-methyl-4-(1-methylethyl)-cyclohexene          | 8.382   | 95  | 0.17|
| 8. | 1-methyl-4-(1-methylethyl)-cyclohexanol         | 8.487   | 93  | 0.15|
| 9. | 2-octanal (E)                                   | 8.983   | 93  | 0.21|
| 10.| 1-octanol                                       | 9.215   | 97  | 0.35|
| 11.| Nonanal                                         | 9.828   | 99  | 3.09|
| 12.| 2-nonenal (E)                                   | 10.790  | 96  | 0.28|
| 13.| Cis-4-Decenal                                   | 11.404  | 88  | 0.18|
| 14.| Decenal                                         | 11.553  | 97  | 0.17|
| 15.| 2-Decenal (E)                                   | 12.454  | 94  | 2.97|
| 16.| 2,4-decadial                                    | 13.335  | 95  | 0.38|
| 17.| 1-Eicosanol                                     | 13.855  | 88  | 0.20|
| 18.| 2-Undecenal                                     | 14.097  | 95  | 3.05|
| 19.| Hexadecane                                      | 19.229  | 97  | 0.15|
| 20.| 3-heptadecene, (Z)                              | 20.610  | 96  | 0.35|
| 21.| 1-heptadecene                                   | 20.702  | 96  | 0.16|
| 22.| 3,7,11-trimethyl-1-dodecanol                    | 21.411  | 90  | 0.29|
| 23.| 1-heptadecene                                   | 22.220  | 95  | 0.16|
| 24.| Heneicosane                                     | 22.472  | 96  | 0.18|
| 25.| Hexadecanoic acid, methyl ester                 | 24.074  | 95  | 0.14|

Rt- Retention time, SI-Similarity Index, A%-Relative Area percent
3.3. Analysis of elemental composition

According to the WDXRF analysis of single use plastic bag, the different concentrations of elements were found to be Ti (0.0587 %), Cl (0.0093 %) and Sr (0.0026 %) and so on. The result was shown in Table (5).

Table 5. Relative abundance of elements in single use plastic bag.

| No. | Elements | Relative Abundance (%) |
|-----|----------|------------------------|
| 1   | Ti       | 0.0587                 |
| 2   | Al       | 0.0237                 |
| 3   | K        | 0.0123                 |
| 4   | Si       | 0.0118                 |
| 5   | Mg       | 0.0113                 |
| 6   | Cl       | 0.0093                 |
| 7   | Ca       | 0.0047                 |
| 8   | Cu       | 0.0032                 |
| 9   | Cr       | 0.0029                 |
| 10  | Sr       | 0.0026                 |
| 11  | Fe       | 0.0025                 |
| 12  | Ag       | 0.0019                 |
| 13  | S        | 0.0014                 |
| 14  | P        | 0.0006                 |
| 15  | Zn       | 0.0005                 |
| 16  | Mn       | 0.0002                 |

4. Discussion

The identification of single use plastic bags was done by FTIR and the analyzed spectrum showed the prominent peaks at 2950 cm\(^{-1}\), 2850 cm\(^{-1}\), 1430 cm\(^{-1}\), 1480 cm\(^{-1}\), 875 cm\(^{-1}\), 740 cm\(^{-1}\) and 720 cm\(^{-1}\). These prominent peaks were consistence with those of library spectra. Therefore, the analyzed single use plastic bag samples were identified as Low-Density Polyethylene (LDPE) polymer by comparing with the library spectra. According to GCMS analysis, the total number of released chemicals from single use LDPE plastic bags by using four types of solvents were in the order of olive oil > chloroform > ethanol > water extract. Most of the released chemicals found from these types of extracts were petrochemical related compounds. The separated compounds were identified by base peak and similarity index (SI). In this analysis, some separated peaks were can not identified by library mass spectral data. These unidentified compounds might be by products of known compounds in the libraries.

Dioxin like substances (2,3- dihydro-1,4-dioxin) were only found in ethanol extract of single use LDPE plastic bags (the relative area percent, 3.77 and the retention time, 1.58 minutes). The U.S EPA was recommended that dioxin and dioxin like substances are structurally and toxicologically related[12]. Dioxin has been classified as human carcinogen by International Agency for Research on Cancer (IRAC) and acts as endocrine disruptor [13]. Combination of dioxin like compound with chlorine and heat, it might be changed into human carcinogenic dioxin.

In the elemental composition of single use LDPE plastic bags, titanium element was most abundantly contained according to WDXRF analysis. Titanium element used as a reaction catalyst (TiCl\(_4\)) for initial polymerization of LDPE (Ziegler-Natta reaction) and then a number of plasticizers, lubricants, stabilizing agents, antioxidants and pigments contain elements such as Ti, Mg, Fe, Al, P, Cl, Ca or Cr [14].
5. Conclusion
The study revealed that tested single use LDPE plastic bags are containing of chemicals that are toxic to human beings such as toluene, ethyl benzene, methyl oxirane, supraene and some type of aldehyde, and even carcinogenic dioxin-like substance such as 2,3-dihydro-1,4-dioxin.

When these chemicals come in contact of hot food or drinks, they might be migrated into contact foods and entered into human body through foods and cause various lethal diseases and disturbance in the human body like cancer so it is better to avoid the single use LDPE plastic bags. Now a days when incidence of cancer and hormonal diseases are very common so it is very necessary to spread the awareness about the use and their probable adverse effect of using single use LDPE plastic bags. It is also a high time for authorities to make some stringent policy for the manufacturer of single use LDPE plastic bags and other plastic food containers.

When these chemicals come in contact of hot food or drinks, they might be migrated into contact foods. Long-term exposure to these type s of chemicals can cause various diseases, disturbance the endocrine system and cell function in the human body. So it is better to avoid the single use LDPE plastic bags. Now a days when incidence of cancer and hormonal diseases are very common so it is very necessary to spread the awareness about the use and their probable adverse effect of using single use LDPE plastic bags. It is also a high time for authorities to make the stringent policy to control toxic chemical contamination for the manufacturer of single use LDPE plastic bags and other plastic food containers.

6. Recommendations
To avoid the harmful effect of single use LDPE plastic bags either we should avoid their use with hot foods or use with caution to reduce the exposure of toxic chemicals. Usually single use LDPE plastic bags and other plastic containers carry a recycling symbol on it.

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