

Chromium Metal Migration Analysis on Some Polypropylene Plastic Packaging in the Market

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Abstract. Polypropylene is the type of plastic that is most widely used in daily life, especially for food products, both for packaging, as containers and for use in household appliances such as cups, milk spoons and trays. Contact between plastic and food can cause the migration (transfer) of chemicals from the container to the food. Migratory heavy metals including Pb, Cd, Hg and Cr(VI). Hexavalent chromium metal (Cr (VI) is one of the metals that migrates the most into food packaging. In order to ensure that the packaging or plastic packaging containers are safe, it is necessary to carry out a migration test. Migration testing is carried out using a UV-Vis spectrophotometer. The test results on the three packages showed that the metal content of Cr (VI) in the cup packaging was 0.006367336 mg/L and 0.006384528 mg/L, while the milk spoon packaging was 0.006367336 mg/L and 0.006324356. mg/L. In tray packaging, the values are also almost the same, namely 0.006384528 mg/L and 0.006350144 mg/L. The test results show that all samples met the BPOM standard No. HK 03.1.23.07.11.6664 in 2011 which stated that the detection limit for chromium metal migration was 1 mg/L.

Keywords: Plastic packaging; Migration; Hexavalent Chromium and UV Vis Spectrophotometer.

1 Introduction

Packaging is one of the most important things in the food industry. Food products require packaging. In order to keep the product clean, avoid physical damage and prevent contamination by microorganisms or from chemical damage (eg gas permeation, moisture/water vapor). Besides that, packaging functions to place a processing product or industrial product so that it has forms that make it easier for storage, transportation, and distribution [1]. Product packaging is also one of the main attractions for consumers, it can even be a reason for a consumer to buy the product. In other words, packaging is an important factor in selling a product.

The packaging materials used today vary from plastic, cans, glass, glass, paper, cardboard, and others. However, in everyday life, the packaging that is often used as a food or beverage container is plastic packaging. The use of plastics as food packaging according to regulations (BPOM No. HK 03.1.23.07.11.6664) in 2011 is divided into various types, namely: Polyethylene Terephthalate (PET), High Density Polyethylene (HDPE), Polyvinyl Chloride (PVC), Low Density Polyethylene (LDPE), Polypropylene (PP), Polystyrene (PS) and others

such as Polycarbonate (PC). Plastic packaging is widely used because it has the advantages of being air and watertight, more elastic, not easy to leak, anti-rust and resistant to chemicals and cheaper processing costs.

Plastic packaging is made of chemical compounds, if the use is not appropriate, there will be migration of substances contained in plastic and have a negative impact on health. Migration is a process of moving a substance from food packaging into food. Migration can have an impact on food quality and safety. From a physical point of view, migration can cause changes to the aroma, smell and taste of the packaged product. Migration can also accumulate in the body which if left for a long time can have an impact on human health.

Under certain conditions, contact between plastic and food can cause the migration (transfer) of chemicals from the container to the food. Migration occurs due to the influence of hot food temperature, storage time, and processing. The higher the temperature, the higher the possibility of migration [2]. The length of time food storage also affects the transfer of this chemical-based material. The longer the contact between food and plastic packaging, the higher the amount of chemicals that migrate to the food. If this happens continuously will interfere with health and will increase the risk of cancer and several other dangerous diseases. At room temperature, with a sufficiently long contact time, small molecular weight compounds can enter food freely, both from additives and plasticizers. The migration of monomers as well as polymerization auxiliaries, in certain levels can dissolve into solid food or oily liquid or non-oily liquid [2]. The hotter the packaged food, the higher the chance of migration (migration) because monomers can migrate into the food and pose a health risk and if accumulated in the body, in large quantities endanger the health of consumers.

In addition to the migration of monomers and polymerization aids, heavy metals such as Pb, Cd, Hg, Cr (VI) can also migrate into the packaging [3]. Chromium metal (Cr (VI)) is one of the metals that migrates the most into food packaging [4]. Usually the metal is added as a mixture of dyes on the packaging. Packaging containing chromium will have an impact on health because it has a toxic effect. Chromium metal is a chemical that is persistent, bioaccumulative, toxic (Persistent, Bioaccumulative and Toxic (PBT)) cannot be decomposed in the environment, and is carcinogenic. Chromium carcinogenicity is usually caused by hexavalent chromium 5 (Cr(VI)) which is corrosive and insoluble in water. Cr(VI) can also cause open sores (irritants) to the nasal passages and skin.

In order to control the contamination of food products in plastic packaging and avoid the negative impacts caused, the government has set special standards in the form of supervision or certain limits for food product packaging, which are the reference for providing food product packaging that is safe and healthy for consumption [5]. Therefore, it is necessary to test the migration on plastic packaging circulating in the market, especially for food packaging. The plastic that is often used for food packaging is plastic with polypropylene (PP) material..

2 Research Methods

Testing the metal content of hexavalent chromium Cr (VI) was carried out by preparing a sample to be tested with a size of 200cm² and then entering it into an Erlenmeyer. Then add 100 ml of 4% acetic acid simulant at 60°C. Store in the oven at 60°C for 30 minutes. The next step is to separate the test sample with 4% acetic acid solution by transferring the 4% acetic acid simulant water that has been in contact with the sample into the test bottle. Furthermore, measurements with a UV-Vis spectrometer were carried out by preparing a standard solution.

Standard solutions were prepared by diluting 4% acetic acid to a concentration of 5 ppm in 100 mL. The dilution was continued by diluting the concentration of 5 ppm with 4% acetic acid to a concentration of 0.01 ppm, 0.02 ppm, 0.03 ppm, 0.04 ppm, 0.05 ppm in 100 mL. Next, add 2 mL of diphenylcarbazide solution and then homogenize. Then the absorbance was measured using UV-Vis spectrophotometry with a wavelength of 540 nm.

3 Results and Discussion

In carrying out the migration test for Cr(VI) metal in packaging using the spectrophotometric method, it is necessary to determine the calibration curve as a standard in calculating the Cr (VI) content of the packaging. The steps start by making a standard solution. The standard solution was prepared by dilution of 50 ppm Cr(VI) metal mother liquor to 5 ppm. Then the 5 ppm solution was diluted again into a solution with a concentration of 0.01; 0.02; 0.03; 0.04; 0.05 mg/L. After that, diphenylcarbazide was added and stirred [6-8], then allowed to stand for 10-15 minutes for optimum color change to occur, then the absorbance of the standard solution was measured using a UV-Vis spectrophotometer at a wavelength of 540 nm. Stirring aims to make a homogeneous solution. The standard solution and the observed sample were first colored with diphenylcarbazide color reagent so as to produce a violet colored compound that could be observed with a UV-Vis spectrophotometer.

The results of measuring the absorbance of Cr (VI) with a UV-Vis spectrophotometer at various concentrations for the calibration standard curve can be observed in Table 1. Furthermore, after obtaining absorbance data from the concentration of the standard Cr (VI) series solution, a standard curve is made between the concentration of the solution and the absorbance . The standard curve was made with the aim of knowing the relationship between the concentration of the solution and its absorbance value so that the concentration of the sample can be known [9]. From the data obtained, a curve can be made as shown in Figure 1.

Table 1. Absorbance of Cr(VI) at various concentrations.

Concentration (ppm)	Absorbance (a.u)
0.00	0.00
0.01	0.01
0.02	0.02
0.03	0.03
0.04	0.04
0.05	0.05

Based on Figure 1, the linear equation is obtained, namely $y = ax + b = 0.8596x + 0.0058$ which is the relationship between the concentration (x) of the standard solution and the absorbance (y), with a correlation coefficient (R) of 0.9997. The value of R shows that the calibration curve has an accuracy in determining the concentration of Cr (VI) of 99.97% and the curve is in accordance with the Lambert-Beer law where the curve of the relationship between absorbance and concentration is a straight line. The metal content of Cr (VI) in the sample can be obtained by substituting the absorbance value of the sample in the linear equation.

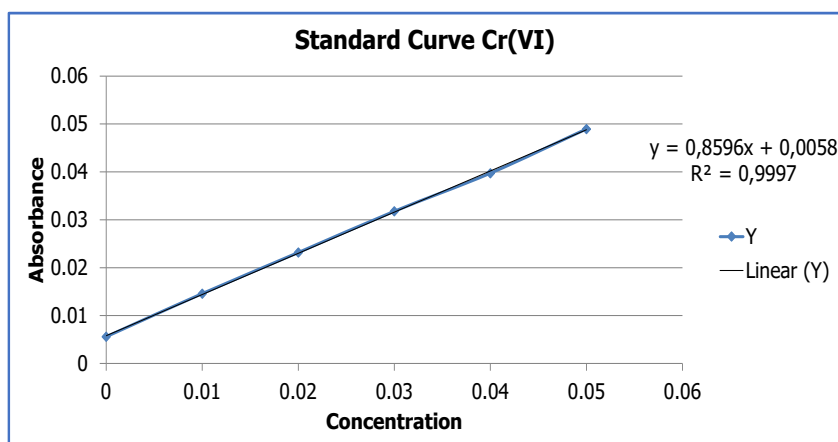


Fig. 1. Standard Curve Cr(VI).

Based on Figure 1, the linear equation is obtained, namely $y = ax + b = 0.8596x + 0.0058$ which is the relationship between the concentration (x) of the standard solution and the absorbance (y), with a correlation coefficient (R) of 0.9997. The value of R shows that the calibration curve has an accuracy in determining the concentration of Cr (VI) of 99.97% and the curve is in accordance with the Lambert-Beer law where the curve of the relationship between absorbance and concentration is a straight line [10]. The metal content of Cr (VI) in the sample can be obtained by substituting the absorbance value of the sample in the linear equation. After making the standard curve, the sample is tested. The first thing to do is sample preparation using 4% acetic acid which has been heated to a temperature of 60°C. In testing the migration of Cr (VI) metal, there are three test methods, namely the cell method, immersion and filling method. For testing cup packaging using the filling method, which is filling the cup using 10 ml of 4% acetic acid solution. As for testing the milk spoon and tray packaging, the immersion method was used, namely by cutting the package with a size of 10 cm x 10 cm then dipping the piece into 10 ml of 4% acetic acid solution in a glass beaker and then stirring it. Furthermore, all samples were evaporated in an oven at 60°C for 30 minutes. Finally, the solution was transferred into a cuvette to be tested for chromium metal using a UV-Vis Spectrophotometer instrument, as shown in Figure 2.



Fig. 2. UV-Vis Spectrophotometer instrument.

In the UV-Vis spectrophotometric testing stage, first prepare a blank solution, the blank solution used is the blank of the solvent used to dissolve the sample, namely distilled water. The blank solution was used as a control spectrophotometer in the experiment in the form of distilled water. Aquades as the solvent will reach the zero point because the water itself contains compounds, these compounds will affect the absorption of the absorbance so that the content of distilled water and in it is ignored, so the concentration starts from the zero point.

The sample was then measured its absorbance using a UV-Vis spectrophotometer by taking 1 ml of the sample. Next, measure the absorbance with a UV-Vis spectrophotometer at the maximum wavelength obtained, the results are as shown in Table 2. The reason for using the maximum wavelength is because at that maximum wavelength the sensitivity is also maximum because the change in absorbance for each unit of concentration is the largest [10]. The test results on the three packages showed that the absorbance values in the cup packaging were 0.0066 and 0.0068 while the size of the milk spoon packaging was 0.0066 and 0.0061. In the tray packaging the values are also almost the same, namely 0.0068 and 0.0064.

Table 2. Absorbance of Cr(VI) at various concentrations.

Sample	Absorbance (a.u)
Cup (A)	0.0066
Cup (B)	0.0068
Spoons Milk (A)	0.0066
Spoons Milk (B)	0.0061
Tray (A)	0.0068
Tray (B)	0.0064

The metal content of Cr (VI) in the sample can be obtained by substituting the absorbance value of the sample in the linear equation obtained from the calibration curve of the standard solution, namely $y = ax + b = 0.8596x + 0.0058$. The results of the measurement of the content of Cr (VI) can be observed in Table 3.

Table 3. Absorbance of Cr(VI) at various concentrations.

Sample	Absorbance (a.u)	Explanation
Cup (A)	0,006367336	According to standard
Cup (B)	0,006384528	According to standard
Spoons Milk (A)	0,006367336	According to standard
Spoons Milk (B)	0,006324356	According to standard
Tray (A)	0,006384528	According to standard
Tray (B)	0,006350144	According to standard

The test results on the three packages showed that the metal content of Hexavalent Chromium (Cr (VI)) in the cup packaging was 0.006367336 mg/L and 0.006384528 mg/L, while the milk spoon packaging was 0.006367336 mg/L and 0.006324356. mg/L. In tray packaging, the values are also almost the same, namely 0.006384528 mg/L and 0.006350144 mg/L.

Based on the results of the analysis carried out on the Cr(VI) parameter in the cup, milk spoon and tray packaging, it showed that all samples met the BPOM No. standard. HK 03.1.23.07.11.6664 [5] of 2011 which states that the detection limit for chromium metal migration is 1 mg/L. Detection limits are obtained from analysts who use calibrated equipment under conditions designed in such a way that they differ from routine testing activities. Based on the test results, the sample passed the chrome test. However, it cannot be said to be safe because it needs further heavy metal testing such as heavy metal test for lead (Pb), cadmium (Cd), mercury (Hg) using different instruments.

The impact that occurs when the sample contains hexavalent chromium (Cr (VI)) with a value exceeding the limit is that it can cause various health effects [11-13]. The accumulation of Hexavalent Chromium (Cr (VI)) in large quantities in the human body is very disturbing to health, because Hexavalent Chromium (Cr (VI)) has a negative impact on the liver, kidneys and is toxic to the protoplasm of living things, besides that it has a carcinogenic effect (cancer-causing), teratogens (inhibits fetal growth and mutagens) [14,15].

4. Conclusion

The study of the migration of Hexavalent Chromium Cr(VI) for cup, milk spoon and tray packaging using a UV-Vis spectrophotometer has been successfully carried out. The calibration curve as a standard in calculating the Cr (VI) content of the packaging has also been determined and produces a linear equation, namely $y = ax + b = 0.8596x + 0.0058$ which is the relationship between the concentration (x) of the standard solution and absorbance (y), with a correlation coefficient (R) of 0.9997. The value of R shows that the calibration curve has an accuracy in determining the concentration of Cr (VI) of 99.97% and the curve is in accordance with the Lambert-Beer law where the curve of the relationship between absorbance and concentration is a straight line. The metal content of Cr (VI) in the sample can be obtained by substituting the absorbance value of the sample in the linear equation, so that the metal content of Hexavalent Chromium (Cr (VI)) in cup packaging is 0.006367336 mg/L and 0.006384528 mg/L while the size of the milk spoon packaging is 0.006367336 mg/L and 0.006324356 mg/L. In tray packaging, the values are also almost the same, namely 0.006384528 mg/L and 0.006350144 mg/L. These results indicate that all samples meet the BPOM No. HK 03.1.23.07.11.6664 of 2011 which states that the detection limit for chromium metal migration is 1 mg/L.

References

- [1] Sucipta, I. N., Suriasih, K., & Kencana, P. K. D.: Pengemasan pangan kajian pengemasan yang aman, nyaman, efektif dan efisien. Udayana University Press Bali, Indonesia (2017)
- [2] Irawan, S. and Supeni, G.: Karakteristik Migrasi Kemasan Dan Peralatan Rumah Tangga Berbasis Polimer. Jurnal Kimia dan Kemasan. Vol. 35, no. 2, pp.105-112 (2013)
- [3] Andrieti, R.: Kemasan Pangan. Kementerian Perindustrian Balai Besar Kimia Dan Kemasan, Indonesia (2018)
- [4] Supeni, G. and Syamsudin, S.: Pengaruh Logam Berbahaya Terhadap Kualitas Kemasan Plastik. Jurnal Kimia dan Kemasan. pp.1-9 (2003)
- [5] BPOM.: Badan Pengawasan Obat dan Makanan No. HK 03.1.23.07.11.6664 Tentang Pengawasan Kemasan Pangan. Jakarta: BPOM: Kemasan Pangan (2011)
- [6] McCort-Tipton, M., & Pesselman, R.: What Simulant is Right for My Intended End Use? (e. S.J.Risch, Ed.) In: Food PAckaging. Testing Methods and Applications (1999)

- [7] Pratiwi, R.: Pengembangan Metode Penentuan Kadar DEHP dan Analisis Migrasi DEHP ke Dalam Simulan Pangan di Pusat Riset Obat dan Makanan. BADAN POM RI: Institut Pertanian Bogor, Indonesia (2010)
- [8] SNI.: In 8.-2. 2007, Cara Uji Migrasi Total dan Kemasan Pangan - Bagian 2: Kemasan Plastik. Jakarta: SNI, Indonesia (2017)
- [9] Castle, L.: An introduction to chemical migration from food contact materials. *International Food Safety News*, Vol. 9, pp. 2-4 (2000)
- [10] Rahmayanti, H.D and Aji, M.P.: Synthesis of sulfur-doped carbon dots by simple heating method. *Advanced Materials Research*. Trans Tech Publications. Vol. 1123, pp. 233-236 (2015)
- [11] McLean, J. E., McNeill, L. S., Edwards, M. A., and Parks, J. L.: Hexavalent chromium review, part 1: Health effects, regulations, and analysis. *Journal-American Water Works Association*. Vol. 104, no. 6, pp. 348-357 (2012)
- [12] Tziritis, E., Kelepertzis, E., Korres, G., Perivolaris, D., and Repani, S.: Hexavalent chromium contamination in groundwaters of Thiva basin, central Greece. *Bulletin of Environmental Contamination and Toxicology*. Vol. 89, no. 5, pp. 1073-1077 (2012)
- [13] Jahrman, E. P., Seidler, G. T., and Sieber, J. R.: Determination of hexavalent chromium fractions in plastics using laboratory-based, high-resolution X-ray emission spectroscopy. *Analytical chemistry*. Vol. 90, no. 11, pp. 6587-6593 (2018)
- [14] Lestari, I., Sapitri, R. A., Gusti, D. R., and El Achaby, M.: The Potential of Cellulose from the Sugar Palm (*Arenga Pinnata*) Seed Shell for Removal of Cr (Vi) Ions. *Journal of Fibers and Polymer Composites*. Vol. 1, no. 1, pp. 52-65 (2022)
- [15] Luo, M., Huang, S., Zhang, J., Zhang, L., Mehmood, K., Jiang, J., and Zhou, D.: Effect of selenium nanoparticles against abnormal fatty acid metabolism induced by hexavalent chromium in chicken's liver. *Environmental Science and Pollution Research*. Vol. 26, no. 21, pp. 21828-21834 (2019)