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Macroplastic and Microplastic Analysis of Marine Fish and Aquatic Fish Using the Fourier Transform Infrared Spectrophotometry (FTIR) Method

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Abstract:
Microplastic is a plastic particle that has a diameter of around 5 μm. The lower limit of the particle size included in the microplastic group has not been defined exactly, but most studies take particle objects with a minimum size of 330 μm^3. In this review article discusses macroplastic types and characteristics of microplastic polymers that are found in marine fish and aquatic fish using the FTIR method. This study aims to examine the scientific literature related to microplastic research using the FTIR method. The method of work uses literature study by finding sources or literature in the form of primary data in the form of official books and international journals in the last 10 years (2010 - 2020). The results obtained are polymers which are found in polyethylene, polyester, polypropylene, PVC, polyethylene terephthalate, and polystyrene. Conclusion: Overall analytical methods to identify the characteristics of microplastic polymers using FTIR, because FTIR has the advantage which it can be used at all light source frequencies, so that analysis becomes faster, FTIR sensitivity is 80-200 times higher than standard disperse instruments.
Key Word*: microplastic; FTIR; marine fish; aquatic fish*

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I. Introduction

Microplastic is a plastic particle that has a diameter of around less than 5 mm (1). The size of the bottom limit particle that includes the microplastic group has not been defined exactly, but most studies take particle objects with a minimum size of 330 μm^3 (2). Pieces of plastic have several kinds of form and size but commonly their size is less than 5 mm (or about the size such as sesame seeds) is called microplastic, because it is still known as the new study and many things is still unknown about what microplastic is and the effect for the environment (3).

The different microplastic sources caused it to appear in several forms such as pellets, fibers, and fragments in the environment (4). It was estimated that 1900 the fiber per item could can be released during washing, and it was released into aquatic and terrestrial environments through liquid waste and sewage sludge application (5). The microplastic are usually in the form of fragments, films, and fibers (6). This type of microplastic fiber is commonly found in coastel areas because this microplastic waste comes from residential areas that work as fishermen (6). As fiber microplastic come from ropes or fishing gear such as plastic bags used by fisherman that as an item to catch fish (6). Not only from the ropes or plastic bags, microplastics fiber can also come from the waste of the making clothes., ropes, fishing rods, and nets (6).

Microplastics films are easily carried by current waves, due to their low density. The types of microplastics that are basically derived from waste or garbage dumps and shops and food stalls that exist in the environment around the waters. The source of microplastic waste which is found mostly comes from the disposal of plastic bags both large and small plastic bags, rice or Styrofoam packages, ready-to-eat food packages and bottles, plastic drinks. Plastic waste that is discharged into these waters will experience decomposition into small pieces to form fragments (7). Secondary microplastic sources are considered to be a large contributor to microplastic pollution given the large amount of macroplastic waste that pollutes the environment (8).

Secondary microplastics, derived from anthropogenic activities, such as littering and being released during the process of collecting and disposing of solid waste in the city. These large plastics and degraded plastics can enter the water environment through wind, soil erosion. Likewise, lightweight macroplastics and microplastics can get into water assisted by wind, while denser polymers tend to be buried deeper in the soil layer (9).

Film microplastics are easily carried by current waves, due to their low density. The types of microplastics that are basically derived from waste or garbage dumps and shops and food stalls that exist in the environment around the waters. The source of microplastic waste which is found mostly comes from the disposal of plastic bags both large and small plastic bags, rice or Styrofoam packages, ready-to-eat food packages and bottles, plastic drinks. Plastic waste that is discharged into the waters will experience decomposition into small pieces to form fragments (7).

Microplastic types can be divided into several types, including:

1. Fiber

Microplastic fiber comes from ropes or fishing gear such as plastic sacks that fishermen use to catch fish. Not only comes from ropes or plastic sacks, microplastic fiber can also comes from the waste of making clothes, ropes, fishing rods, and nets (6).

2. Film

Film is a secondary plastic polymer that comes from plastic bag or plastic bag fragmentation and has a low density. The film has a lower density than other microplastic types so that it is easier to be transported to the highest tide (10).

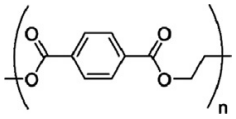
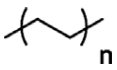
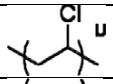
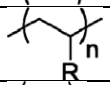
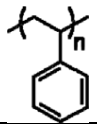
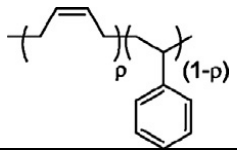
3. Fragments

This type of fragment basically comes from the waste dump or garbage from shops and food stalls in the surrounding environment. These include plastic bags both large and small sized plastic bags, rice wrappers, ready-to-eat food packages and plastic beverage bottles. The plastic waste breaks down into small pieces up to fragment type (10).

4. Granules

Types of granules generally come from plastic factories. Microplastic types are granules and are white or brown, solid. Granules are small particles used for industrial products (10)

Table 1. Examples of polymers and absorption bands (cm^{-1}) used for identification (11)

Polymer	Chemical Structure	Absorption bands (cm^{-1}) that **be** used for identification
Polyethylene terephthalate (PETE)		1713 (a) 1241 (b) 1094 (c) 720 (d)
High-density polyethylene(HDPE)		2915 (a) 2845 (b) 1472 (c) 1462 (d) 730 (e) 717 (f)
Polyvinyl chloride (PVC)		1427 (a) 1331 (b) 1255 (c) 1099 (d)966 (e) 616 (f)
Low-density polyethylene(LDPE) or linear LDPE(LLDPE)		2915(a)2845(b)1467(c)1462(d)1377 (e)730 (f)717 (g)
Polypropylene (PP)		2915 (b) 2838 (c)1455 (d)1377 (e) 1166 (f) 972 (h) 840 (i) 808 (j)
Polystyrene (PS)		3024 (a) 2847 (b)1601 (c) 1492 (d) 1451 (e) 1027 (f) 694 (g) 537 (h)
Latex		2960 (a) 2920 (b) 2855 (c) 1167 (d) 1447 (e) 1376 (f)

II. Material And Methods

In arrang**e** this review article, the technique used is using literature study by finding sources or literature in the form of primary data in the form of official books and international journals in the last 10 years (2010 - 2020). In addition, in making this review article the search for data was carried out using online media with keywords namely Microplastic and Macroplastic Analysis of Marine Fish and Aquatic Fish.

III. Result

Various types of macroplastics and characteristics of microplastic polymers found in fish, the most common types of microplastic are fiber type and film type, and for the most common polymer characteristics are PVC, PS, and PP. The primary reference search used in this review article is through trusted web sites such as Science Direct, NCBI, Research Gate, Google scholar and other published and credible journals.

Table 2. Types of Microplastics and Characteristics of Microplastic Polymers found in Fish Based on Several Scientific Articles

No	Samples	Sampling place	Types of Microplastic	Characteristics of Microplastic Polymer	Tool	References
1	*S.gibbosa* *H. translucens* *H. nehereus*	Northern Bengal Bay	Fragment, Fiber, Granule	Polyethylene terephthalate, polyamide	FT-IR	(12)
2.	Small Pelagic Fish	Mediterranean sea	Fiber	polyethylene terephthalate	FT-IR	(13)
3.	*Myripristis sp*	South Pacific Ocean	fiber, fragment, and film	Polyester	FT-IR	(14)
4.	Zebra fish	China Coastal Coast	Fiber	Polyester, polypropylene, polyethylene	FT-IR	(15)
5	*Symbolophorus californiensis, Myctophumaurolanternatum, Loweinainterrupta, Hygophumreinhardtii*	North Pacific Central Gyre	Filament, Pellet, Film	polystyrene	FT-IR	(16)
6	*Trichiurus sp. Johnius sp.*	Pangandaran Bay, Indonesia	Fragment, Fiber, Film	Polyester	FT-IR	(17)
7	*D.labrax, T. trachurus, S. colias*	Northeast Atlantic Ocean	Fiber, Fragments, Pellets	Polyethylene, Polyester, Semisynthetic Cellulose	FT-IR	(18)
8	*Konosirus punctatus, Mugil cephalus*	East coastal areas of Guangdong, South China	Fragments, Fiber, Film, Granules	Polyethylene, polystyrene	FT-IR	(19)
9	*S.japonicus, M.capensis, T. capensis*	South Africa	Fiber, Fragments	Polyester	FT-IR	(20)
10	*C.carpio, C.cuvieri, L.macrochirus, M. salmoides, S.asotus, C.argus*	Han River, South Korea	Fragments, Fiber	polytetrafluoroethylene (PFTE),polyethylene(PE)	FT-IR	(21)
11	*Chelidonichthyskumu, Muraenesoxcinereus, Raja porosa.*	Artificial Reefs Around the Ma'anShengshi Islands, China	Fiber	Polyethylene, Polyester	FT-IR	(22)
12	*Opisthonemaoglinum, Bagre marinus, Cathoropsspixii, Sciadesherzbergii, Chloroscombruschrysurus, Conodonnobilis, Haemulopsiscorvinaeformis*	Urban Beach in Brazil	Filament, Fragment	Polyester	FT-IR	(23)
13	*O. mossambicus. O.mossambicus, T. jarbua, Mugil cephalus, A. dussumieri*	Kwazulu-Natal, South Africa	Fiber, Fragments, Films	Polyester, Nylon, PVC, Polyethylene	FT-IR	(24)

14	*Thryssakammalensis, Amblychaeturichthyshexanema, Odontamblyopusrubicundus, Cynoglossussemilaevis, Chaeturichthysstigmatias and Collichthyslucidus*	Haizhou Bay, China	Fiber, Fragment	Polypropylene, polyethylene, polyester	FT-IR	(25)

V. Discussions

Microplastic is a plastic that has a particle size of 0.33 mm - 5 mm. Nanoplastics have sizes that are even smaller than 0.33 mm and are widely used in treatment materials or cosmetics, such as toothpaste and facial scrub containing plastic in the form of polyethylene glycol abbreviated as PEG. Microplastic is not visible but has the potential to have a negative impact on both biota and water. Human health problems are suspected through microplastic accumulation in the food chain and / or absorption of toxins into the plastic when carried by ocean currents (26).

The work method used also has an important effect when identifying microplastics that have been discovered, such as the use of NaCl. NaCl is used to separate microplastics from non-microplastics based on differences in density (27). NaCl solution has a density of 1.2 g cm^{-3} which is lower than some microplastic polymers (27).

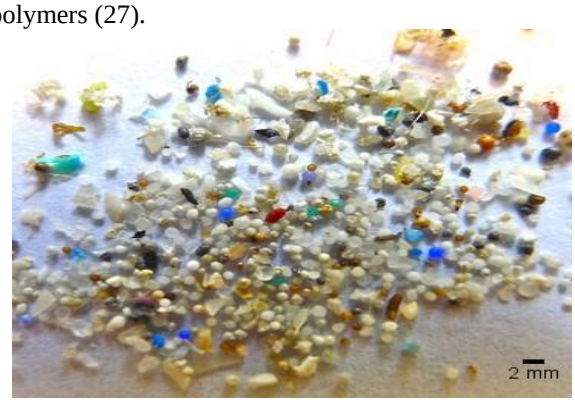


Figure 2.1 Microplastics found in fish (28)

Figure 2.2 Microplastic found in fish (29)

Profile of microplastic form found in fish

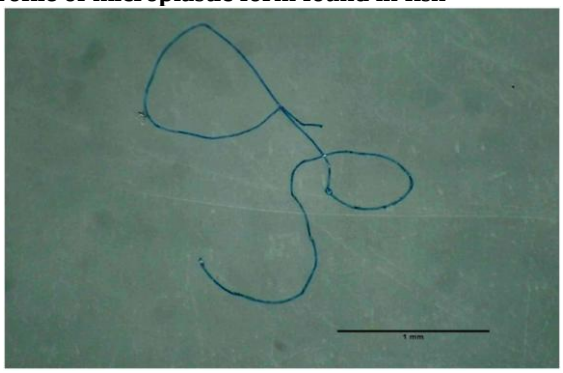


Figure 2.3 Type of Fiber Microplastic (27)

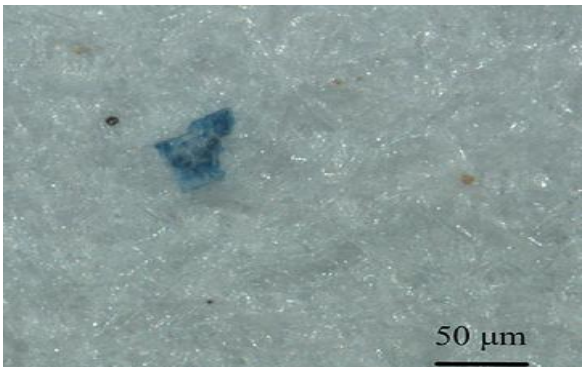


Figure 2.4 Type of Fragment Microplastic (25)

Figure 2.5 Types of Film Microplastic (21)

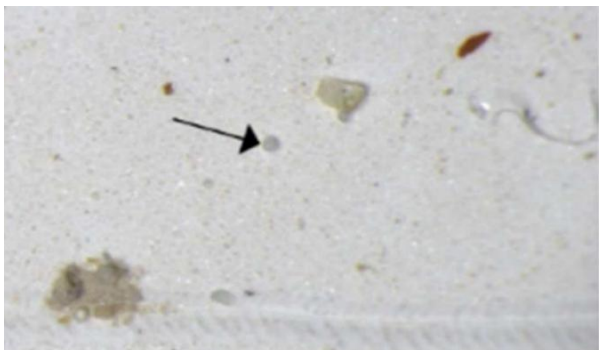


Figure 2.6 Types of Granule Microplastic (21)

Microplastic types that are found in fish are fiber, fragment, film, grain, and pellet. The number of microplastic types found in the form of fiber, fragments, films, grains in fish, this indicates that a lot of waste around the waters and the sea comes from household waste or from fishing nets.

Figure 2.3 shows the type of fiber-shaped microplastic. Microplastics fiber comes from ropes or fishing gear such as plastic sacks that fishermen use to catch fish. Not only comes from ropes or plastic sacks, microplastic fiber can also come from the waste of making clothes, ropes, fishing rods, and nets (6).

Figure 2.4 shows the microplastic type of fragment form, the type of fragment comes from the waste disposal or rubbish from shops and from food stalls in the surrounding environment. These include plastic bags both large and small sized plastic bags, rice wrappers, ready-to-eat food packages and plastic beverage bottles. The plastic waste breaks down into small pieces up to fragment type (10).

Figure 2.5 shows the type of film-shaped microplastic, film type is a secondary plastic polymer derived from plastic bag fragmentation or plastic packaging and has a low density. The film has a lower density than other microplastic types so that it is easier to be transported to the highest tide (10).

Figure 2.6 shows the microplastic types of granules or granules, granules or granules generally come from plastic factories. Microplastic types are granular and white or brownish, solid. Granules are small particles used for industrial products (10).

In Table 2.2 we can see the characteristics of microplastic polymers that are found in aquatic and marine fish are polyethylene, polyester, polypropylene, PVC, polyethylene terephthalate, polystyrene. Polyethylene Terephthalate is widely used in making beer bottles, water bottles, fiber. Polyvinyl chloride is widely used in making shampoo bottles, construction pipes, toys. Polypropylene is widely used in making medicine bottles, sauce bottles, margarine containers, yogurt containers. Polystyrene is widely used in making disposable cups, CD cases, egg storage areas, and is found in Styrofoam. FT-IR (Fourier Transform Infra Red) spectroscopy is one of the instruments that uses the principle of spectroscopy.

Infrared spectroscopy is equipped with Fourier transforms for the detection and analysis of the results of its spectrum (30). Infrared spectroscopy is useful for identification of organic compounds because of its very complex spectrum which consists of many peaks (31). In addition, each functional group absorbs infrared light at a unique frequency. The scheme and flow of the FT-IR spectroscopy tool can be seen in Figure 2.7

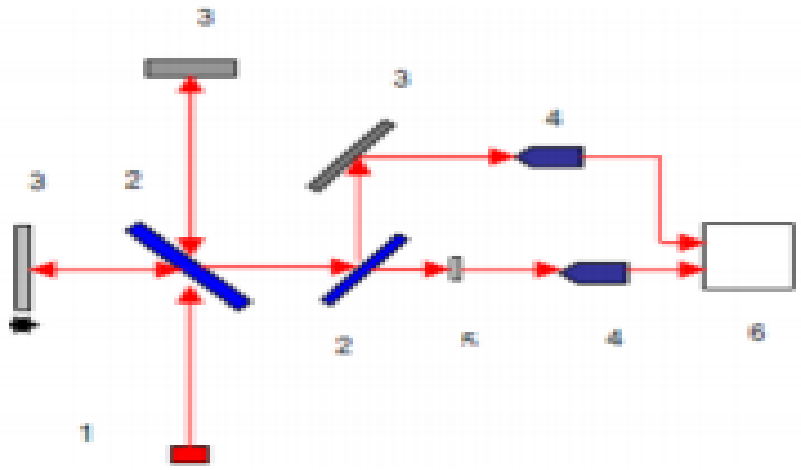


Figure 2.7 FTIR spectroscopy schematic (1) Infrared source. (2) Beam splitters. (3) Reflecting glass. (4) Infrared sensor. (5) Samples. (6) Display (30)

When light passes through a sample, the light transmissions occur so that the infrared spectrum can be seen. Then the incoming light will be measured by the detector, then the incoming light will be compared with the intensity of the light without a sample to measure the wavelength. The infrared spectrum received will be plotted as the intensity of the energy function, wavelength (μm) or wave number (cm^{-1}) (30). In this study, microplastic samples will be observed using FTIR which the purpose is to determine the functional groups contained in the sample and the sample fractions.

Advantages of FTIR Spectroscopy

Analysis using the FTIR spectrometer has several main advantages compared to the conventional methods, which are can be used at all frequencies of a light source simultaneously, so that analysis can be done faster than using scanning (32).

FTIR sensitivity is 80-200 times higher than standard dispersion instrumentation because of its higher resolution. The sensitivity of the FTIR spectrophotometric method is greater than the way of dispersion because more radiation enters the detector system because it does not have to go through a gap (slit less) (32). In FTIR, optical mechanics are simpler with fewer moving parts than other infrared spectroscopy, can identify unknown material, and can determine the quality and number of components in a sample (32).

Some journals use the ATR-FTIR method or micro-Raman spectrometry to identify microplastics that are present in fish, but in most cases, not even up to 10% of particles can be analyzed with ATR-FTIR or micro-Raman spectrometry. Studies conducted in Kuwait and Qatar using micro-Raman and FT-IR on all isolated particles, can only produce very few observable particles, they examine 87 intestinal contents of fish and shellfish, and only three microplastic particles are found in the intestine orange spotted grouper. Therefore many researchers use FTIR rather than ATR-FTIR or micro-Raman spectrometry (27). However, the FTIR method also has weaknesses. FTIR cannot identify the type and content of each fatty acid component of a sample with certainty. Therefore, the results of the FTIR analysis also need to be supported by the results of the GC-MS analysis especially to determine which fatty acid composition is the most dominant of a sample (33)

FTIR Spectrum of Different Types of Microplastics

1. PET (polyethylene terephthalate)

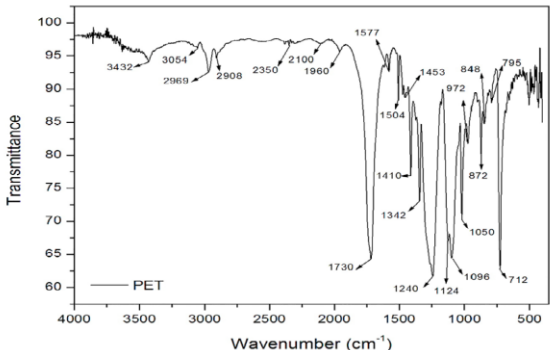


Figure 2.7 FTIR Spectrum of PET (34)

2. HDPE (High Density Polyethylene)

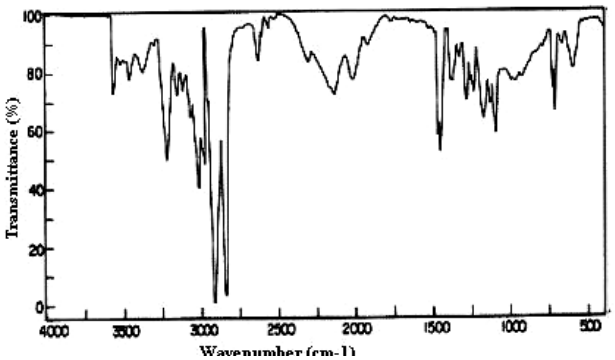


Figure 2.8 FTIR Spectrum of HDPE (35)

3. PP (Propylene)

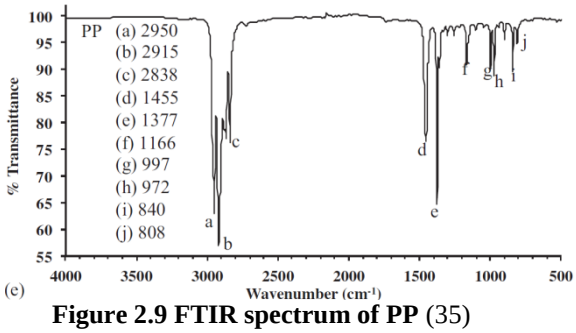


Figure 2.9 FTIR spectrum of PP (35)

4. PVC (Polyvinyl Chloride)

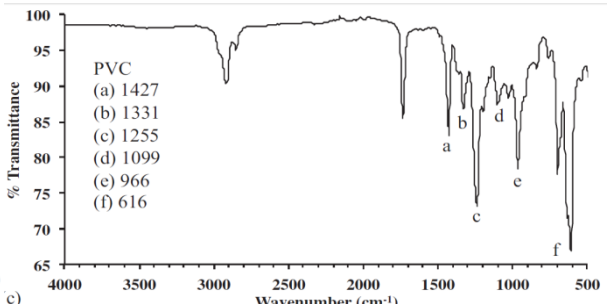


Figure 2.10 FTIR spectrum of PVC (35)

5. LDPE (Low Density Polyethylene)

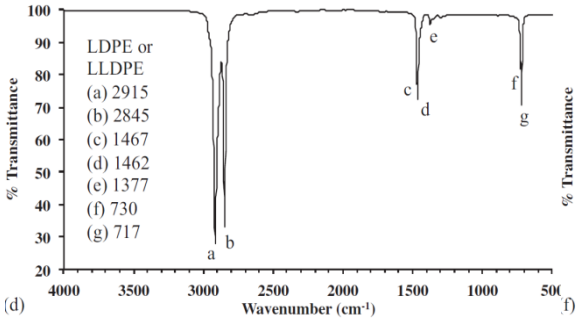


Figure 2.11 FTIR spectrum of LDPE (35)

6. PS (Polystyrene)

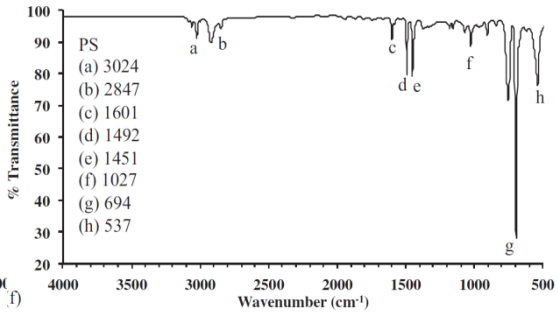


Figure 2.12 FTIR spectrum of PS (35)

7. Latex

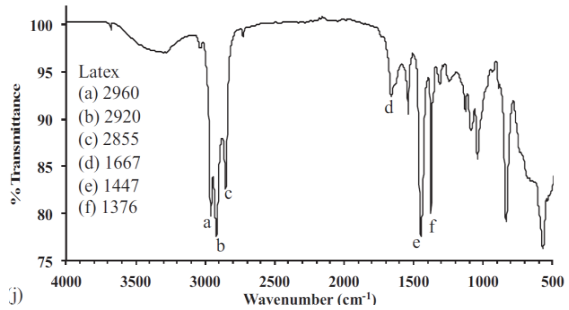


Figure 2.13 FTIR spectrum of Latex (35)

V. Conclusion

Overall, various analytical methods have been used to identify the characteristics of microplastic polymers although the ATR-FTIR or micro-Raman spectrometer method can be used, but analysis using FTIR is more widely used, because FTIR has the advantage that it can be used at all frequencies of light sources, so that analysis becomes faster and FTIR sensitivity is 80-200 times higher than standard disperse instruments. In FTIR, optical mechanics are simpler with fewer moving parts than other infrared spectroscopy, FTIR can also identify unknown materials and can determine the quality of components and the number of components in a sample. Microplastic types that are found in fish are fiber, fragments, films, pellets, and grains. As for the characteristics of microplastic polymers that are commonly found in fish are polyethylene, polyester, polypropylene, PVC, polyethylene terephthalate, and polystyrene.

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