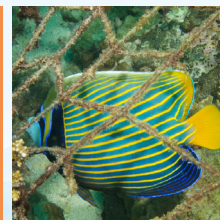


Rapid Polymer Identification of Fishing Gear Using Raman Spectroscopy



Application Note

Microplastics RA82

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Abstract

Plastic pollution from fishing gear is a global problem that harms the environment. Recycling of damaged or abandoned fishing gear is one way of mitigating the issue, however the exact nature of the polymer must be known in order to identify the correct recycling stream. In this paper, the MacroRAM benchtop Raman spectrometer with remote BallProbe® is used to quickly identify plastics used in various gillnet samples. Raman spectroscopy is demonstrated to be an excellent technique for identifying not only different types of polymers, but also different variants within a polymer class and additives including pigments.

Keywords

Microplastics, pollution, environment, polymer, Raman, remote sampling

Introduction

Plastic pollution is a global problem with harmful effects on ecosystems at all levels of the food web. The disposal of fishing gear, specifically, is a large contributor making up approximately 85% of plastic pollution found in marine environments.¹ In addition, nylon fishing line and nets are some of the longest-lived plastics, with lifetimes ranging in the hundreds of years.² To help mitigate the problem of plastic pollution from fishing gear, organizations like *Net Your Problem* collect damaged or abandoned nets, organize and sort them, and ship them to facilities where they may be recycled into pellets for commercial use.³ A critical part of this process is accurately identifying the type of polymer the fishing net is composed of so that it may be sorted into the correct recycling stream (e.g. nylon, polypropylene, polyethylene). Nylon, in particular, can be challenging to identify definitively,++ as there are multiple varieties of nylon that may be used in fishing gear. Unambiguously determining the exact type of nylon is an important step in the sorting process.

Raman spectroscopy has been demonstrated as an excellent technique for distinguishing between various types of polymers and within polymer classes, such as nylon. Raman spectra of nylon are unique enough that a high resolution Raman microscope is not required for

definitive identification. Figure 1 shows spectra of reference nylon materials recorded with HORIBA's MacroRAM benchtop Raman spectrometer. Each of the polymers display clearly distinguishable spectral fingerprints that allow for identification of unknown samples, including abandoned fishing gear.

Experimental Methods

In this study, a set of four monofilament gillnets and one polytwine gillnet were submitted for analysis using Raman spectroscopy (see Figure 2). The samples were collected by the Cape Cod Commercial Fisherman's Alliance and originated from various states in southern New England (Massachusetts, New Hampshire, and Rhode Island).

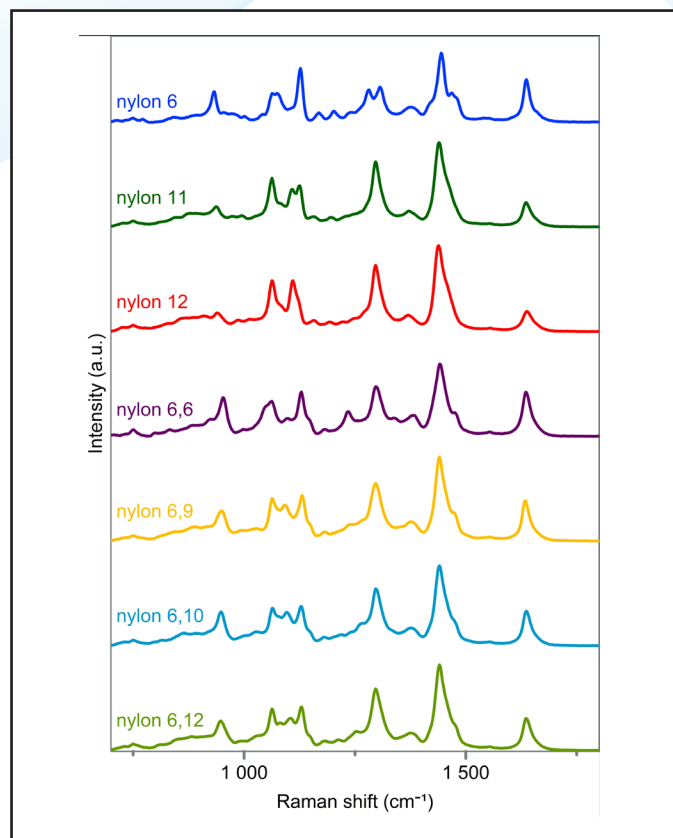


Figure 1: Raman spectra of nylon 6, nylon 11, nylon 12, nylon 6,6, nylon 6,9, nylon 6,10 and nylon 6,12 recorded with HORIBA's MacroRAM benchtop Raman spectrometer. Reference nylon materials were sourced from PolySciences, Inc.

HORIBA's MacroRAM benchtop Raman spectrometer was coupled to a BallProbe® (1/8", MarqMetrix®) to enable rapid, alignment-free Raman characterization and identification of the unknown polymer types. Near-infrared 785 nm laser excitation was employed to suppress fluorescence induced by the pigmented fibers (white, red, green, and blue).

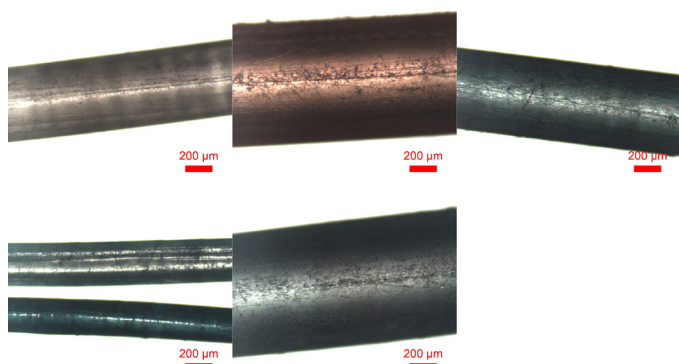


Figure 2: Optical micrographs recorded of various fiber samples; white monofilament gillnet, red monofilament gillnet, green monofilament gillnet, green polytwine gillnet, and blue monofilament gillnet (from top left to bottom right).

Results and Discussion

Spectra recorded from the monofilament samples indicate that all of the samples are comprised of the same variety of nylon. Upon close comparison of the unknown spectra and the nylon reference material spectra, it becomes clear that all of the monofilament samples are assignable as nylon 6. Figure 3 shows the processed spectra of each of the unknown samples after baseline subtraction in addition to the reference spectra of nylon 6 (top) and nylon 6,6 (bottom). In particular, the doublet at $\sim 1300\text{ cm}^{-1}$ is a clear indicator of the assignment to nylon 6 over any other variety of nylon.

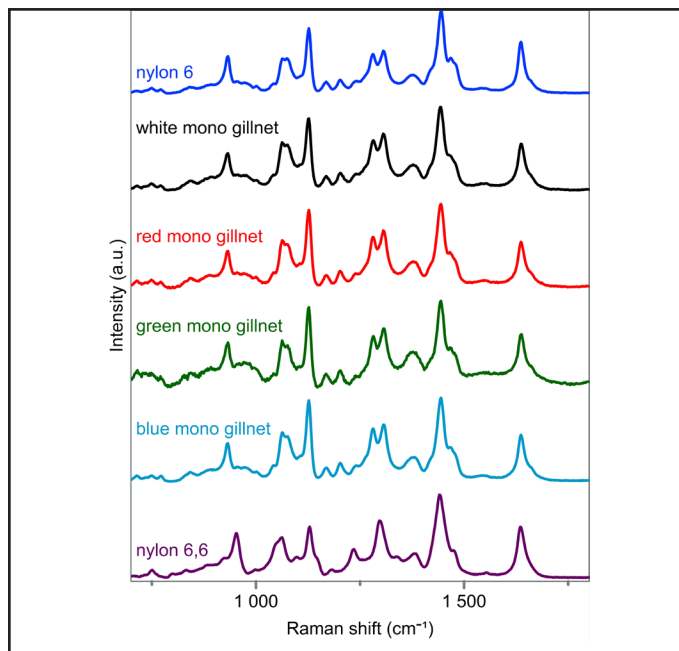


Figure 3: Reference spectra of nylon 6 and nylon 6,6 are shown at the top and bottom, respectively. The spectra of unknown monofilament gillnet samples are plotted in the middle labeled by color (white, red, green, blue).

The green polytwine gillnet sample proved to be more complex. Polytwine gillnets are comprised of multiple filaments interlaced together to form a braid. Upon unravelling the braid, it was clear that there were two different types of filaments making up the polytwine; a lighter colored, slightly thicker set of filaments at the center, and a set of darker color, thinner filaments around the edge. A small sample of each type of filament was trimmed from the polytwine for analysis. Upon measurement of the Raman spectra, it became clear that the same spectral bands were observed in both filaments. However, there was a clear difference in the relative intensities of the Raman bands for the lighter and darker strands, as shown in Figure 4.

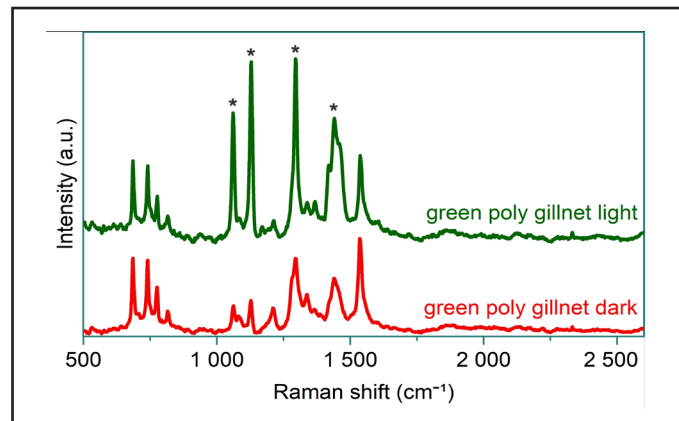


Figure 4: Baseline corrected spectra of light (top) and dark (bottom) colored strands from the green polytwine gillnet sample. The asterisks indicate bands of significantly differing intensity between the two measurements.

Using HORIBA's LabSpec 6 software suite, the spectrum recorded from the darker colored strand was subtracted from the lighter colored strand, and vice versa. The subtracted results revealed spectra that closely matched with polyethylene (light – dark) and pigmosol green (dark – light) as shown in Figure 5 and Figure 6, respectively. In this unknown sample, the polytwine gillnet was not nylon at all, but polyethylene. Despite significant spectral contributions from the pigment, the polymer could easily and confidently be identified.

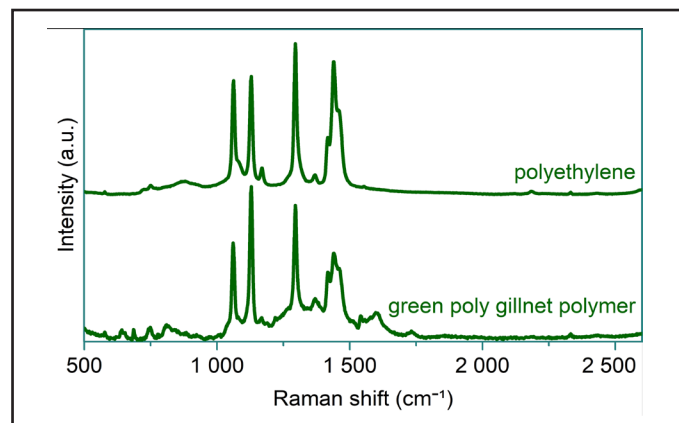


Figure 5: Reference spectrum of polyethylene (top) and subtracted spectrum of the light strand from the green polytwine gillnet sample (bottom).

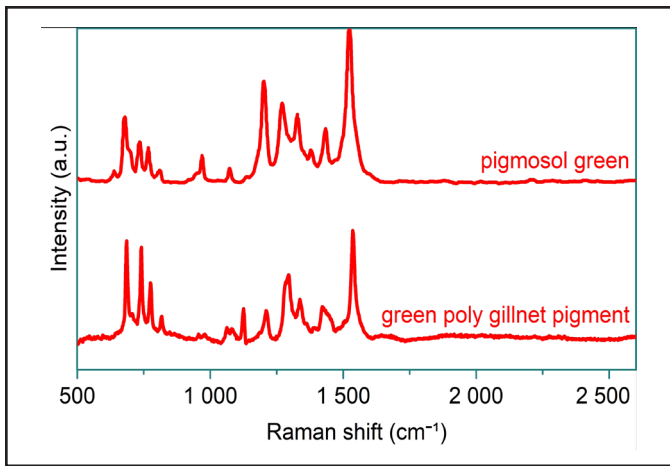


Figure 6: Reference spectrum of pigmosol green from Wiley's KnowItAll software and spectral libraries (top) and subtracted spectrum of the dark strand from the green polytwine gillnet sample (bottom).

While these measurements were performed in a laboratory environment, the results suggest that the MacroRAM could also easily be deployed for field measurements at the site of collection for abandoned nets. Identification can be carried out easily and quickly in real time while sorting through fishing gear and bundling it for shipping using a remote touch probe. In addition, advanced data processing capabilities in LabSpec 6 enable more complex post-acquisition analysis that would not be possible to carry out with simpler handheld Raman devices. Especially for samples with large spectral contributions from pigments, this allows for unambiguous determination of the polymer type.

Lastly, these results are also promising for the measurement of microplastics in a rapid, alignment-free manner. The unknown fiber samples measured in this study ranged

in size from 260 μm to 920 μm in diameter. This is well within the range of the definition of microplastics (<5 mm). Microplastic samples in the range greater than 100 μm in size are routinely hand-picked for observation using a stereo microscope. The addition of a benchtop Raman system coupled to a remote touch probe would provide rapid chemical identification at the point of microplastics sorting and classifying (in size, morphology, and color.) The next advancement would be to deploy the unit in the field to measure microplastics at the source, for example on a coastline or a boat.

Conclusion

The MacroRAM benchtop Raman spectrometer coupled with a remote touch probe provides easy, accurate identification of polymer type from a variety of colored fishing nets. There is not only clear distinction among different polymer classes (polyethylene and nylon) but also within a single polymer class (nylon 6 and nylon 6,6). The methods demonstrated here could be easily expanded for field measurements at the site of abandoned fishing gear or for measurements of microplastics at the source.

Acknowledgements

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- (1) Greenpeace Germany. Ghost Gear: The Abandoned Fishing Nets Haunting Our Oceans; 2019; p 20.
- (2) National Oceanic and Atmospheric Administration. Can marine debris degrade on its own in the environment? <https://oceanservice.noaa.gov/facts/degrade.html> (accessed Apr 15, 2020).
- (3) Nicole Baker. Net Your Problem www.netyourproblem.com (accessed Jul 16, 2020).



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