# Developing ATR-FTIR spectroscopy as a tool for microplastics detection

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Plastic production has reported a considerable increase in recent years since it has become an indispensable aspect of our lives, due to its low manufacturing costs and physicochemical properties. Global plastic production will reach 33 billion tons by 2050, whereas only in 2022, until today, approximately 1.5 trillion plastic bags have already been produced. Accounting for more than 80% of total plastics demand, the most common plastics, comprise commodities polymers such as polypropylene (PP), high- and low-density polyethylene (LDPE, HDPE), polystyrene (PS), and poly(ethylene terephthalate) (PET). Despite the fact that large part of plastic waste is incinerated or subjected to landfill, plastics huge production rates and inadequate waste management have caused a high accumulation of their fragments, consisting of macroplastics, microplastics and nanoplastics, in all available environment matrices spanning from land to air and the ocean [1].

Representing major proportion among plastic fragments, microplastics (plastic particles smaller than 5 mm) originate from the fragmentation of conventional non-biodegradable and biodegradable polymers due the effect of heat, UV radiation, humidity, atmospheric oxidation and weathering. Microplastics are generally classified into two types: primary and secondary, with respect to their origin [2,3]. Primary microplastics are plastic particles produced directly in microplastic form and include microbeads found in personal care products, plastic pellets used in industrial manufacturing, fibers used in synthetic textiles. This kind of particles has direct access to the environment, through various channels (e.g. personal care products being washed into wastewater systems from households, unintentional loss from spills during manufacturing or transport, or abrasion during washing). Secondary microplastics originate from the breakdown of larger plastics, which typically is caused by weathering and degradation, entering the environment as mismanaged or improperly disposed waste.

Biobased and biodegradable polymers, such as PBS and PLA, also undergo fragmentation during their disposal thus being more and more responsible for generating also microplastics. Even more, a new class of biobased polymers will emerge in the future, the biobased vitrimers. Vitrimers are a new class of dynamically crosslinked polymers that involve reversible covalent bonds within the network structure which will allow the recycling/reprocessing of thermosets after their use [5]. While biobased vitrimers (vitrimers based on PLA and PBS) show significant potential and commercial interest towards bridging the gap between thermosets and thermoplastics, their biodegradability might be decelerated due to their crosslinked structure.

A number of research has documented qualitative and quantitative measurements of microplastics throughout the world in all environmental compartments including water, atmosphere, sediment, soil, sewage sludge, biota, and foodstuff. The current work is focused on assessing the validity of ATR-FTIR spectroscopy, since it's a rapid, simple, and cost-effective technique, in order to perform qualitative identification of microplastics in source-separated biowaste. Composting is one the main valorisation options for biowaste. Since the end-product, compost is used as soil amendment or organic fertiliser, there is a need to identify both qualitatively and quantitatively microplastics in this waste stream and to set the pertinent compost specifications in terms of microplastics content. To the best of our knowledge, the percentage of contaminants from microplastics is rarely cited in compost labels. Our methodology involves two steps: 1) vibrational spectroscopy studies on reference virgin polymers and their mixtures, 2) vibrational spectroscopy studies plastic fragments isolated from source-separated biowaste after chemical digestion.

For this purpose, in an early phase, pure polymeric materials in the form of films or flakes ($d < 500$ μm) are examined to collect spectra, recognizing different characteristic wavenumber peaks per polymer type. The polymers specified for this work, are based on both bio- and fossil-based polymers (PLA, PBS, PET, LDPE, HDPE, and PA) that are usually found in common packaging and whose microplastic particles are more likely to be found in urban biowaste (Figure 1). PBS-based vitrimers are also examined as promising materials with enhanced barrier properties.

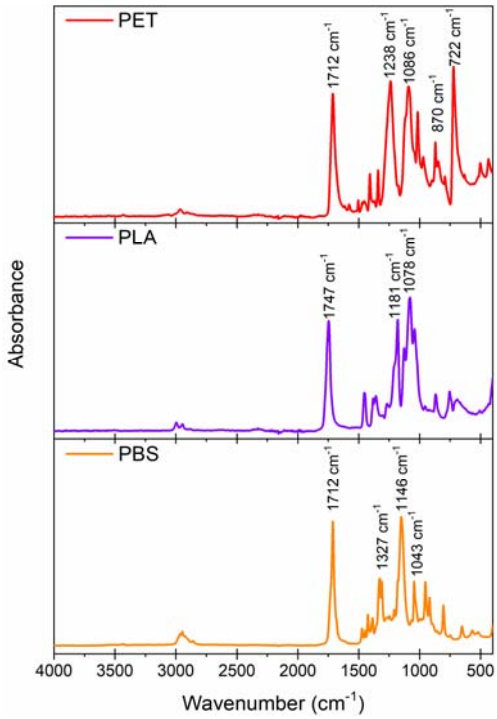


Figure 1: ATR-FTIR spectra of three common polyesters (PET, PLA, PBS) in the form of flakes

Based on the pure polymers, a variety of mixtures is also prepared and characterized through ATR-FTIR spectroscopy aiming to identify the characteristic peaks per polymer type in each mixture and to use the relevant spectra as reference ones (Figure 2).

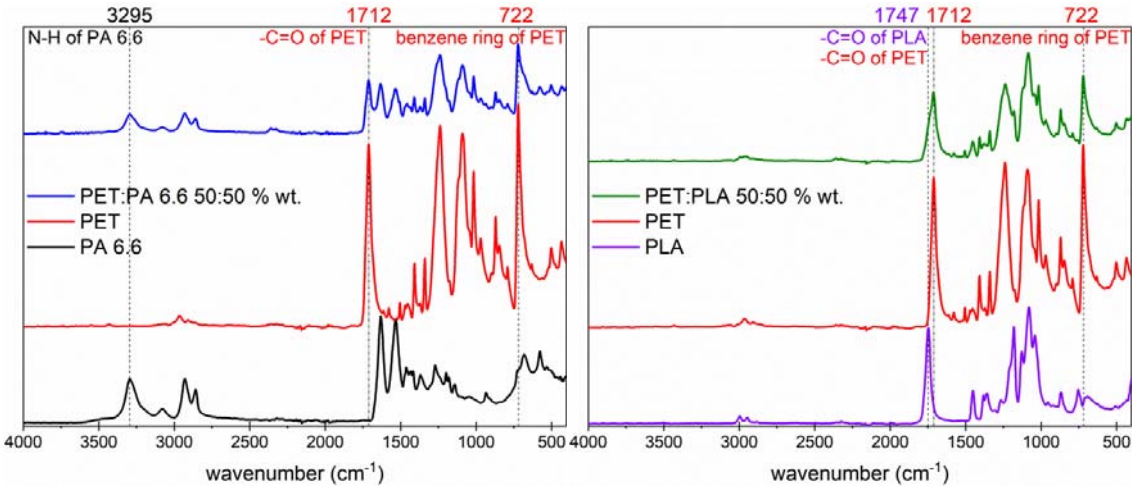


Figure 2: ATR-FTIR spectra of **a)** mixture of PET and PA 6.6 flakes and **b)** a mixture of PET and PLA flakes

Furthermore, dried source separated biowaste of known chemical composition was subjected to chemical digestion in order to isolate the polymeric constituents. From a gravimetric analysis, it was revealed that 4% w/w polymeric materials were included in this waste stream, taking also into consideration the ash content. The residue was subjected to ATR-FTIR, in order to identify the polymeric materials. DSC and TGA were also applied to accumulate more information about the residue. A correlation between the relative band intensities of the spectra of the polymer mixtures and the biowaste residue is attempted.

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