doi:10.2533/chimia.2019.841 Chimia 73 (2019) 841–843 © Swiss Chemical Society

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Universities of Applied Sciences

Fachhochschulen – Hautes Ecoles Spécialisées

Microplastics – from Anthropogenic to Natural

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Abstract: In the context of the ongoing discussion of accumulating plastic debris in the environment, this article summarizes recent reports on the topic of microplastic pollution. Moreover, it gives an overview of the results from the activities of the research group for Biotechnology and Sustainable Chemistry of the Institute of Life Technologies at the HES-SO Valais-Wallis concerning the fabrication of biodegradable microstructured plastics and microplastics from renewable resources. Polyhydroxyalkanoate biopolyesters are proposed as one suitable alternative in specific applications to reduce the use of persistent plastics. Standard techniques are described that have been successfully applied to produce porous materials, fibers and particles in the micro- and nanometer range.

Keywords: Biopolymers · Electrospinning · Microplastics · Nanoparticles · Polyhydroxyalkanoates

1. Introduction

In the current discussion on microplastics, much of the focus is placed on plastic particles smaller than 5 mm, which is in agreement with the technical definition of the EU Ecolabel for detergents and cleaners.[1] Considered are solid and non-water soluble macromolecular plastics. These particulates are further classified as primary or secondary microplastics, depending on whether they are manufactured and used in dimensions of less than 5 mm or plastic parts originating from larger objects that degraded by decomposition and decay processes into smaller pieces.[2] Thus, macroscopic plastic packaging may be a source of microplastics due to exposure to sunlight and mechanical forces or a car tire might lead to microplastics due to road friction.

The emission of synthetic plastic microparticles, referred to as microplastics, has been described in the context of marine pollution for more than 40 years.[3] It is suspected to lead to intestinal dysfunction in higher marine organisms as well as representing a general hazard due to the accumulation of pollutants and bacterial overgrowth.[3]

A study conducted by the Swiss Federal Office of the Environment (FOEN), on plastic pollution in Swiss lakes, identified the synthetic polymers polyethylene and polypropylene as major components of microplastics (followed by polystyrene and cellulose acetate).

The chemical substances phthalates, polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), nonylphenols (NPs) as well as polychlorinated biphenyls (PCBs) were detected as contaminants of the collected microplastics. These substances are either used as additives in plastics manufacturing or water pollutants that concentrate to different amounts in microplastics depending on the polymeric material and the specific surface area (*i.e.* total surface area per unit of mass).

Upon analysis of polyethylene particles collected from surface waters, primarily OCPs and PAHs were found. Their concentration depended on the specific surface of the particulates and presented up to six times higher values for microplastics than for plastic parts with a diameter larger than 5 mm.[4]

While the composition and pollution of microplastics can be analyzed with high accuracy, the origin of the microplastics found in the environment is often uncertain and needs to be estimated from emission assessments.[5] Following this approach, the German Fraunhofer Institute for Environmental, Safety, and Energy Technology (UMSICHT) proposed a top-down approach to identify the origin of microplastics based on production and consumer information in a recent consortium study.[6]

According to their results, the ten major sources of microplastics in Germany are:[7] Abrasion of tires (30.7%), emissions from waste disposal (7.6%), abrasion of polymers and bitumen in asphalt (5.7%), pellet loss (4.6%), windblown dispersal from sports and playgrounds (3.3%), emission from construction sites (2.9%), abrasion from shoe soles (2.7%), plastic packaging (2.5%), road marking (2.3%) as well as abrasion from textiles during laundry (1.9%).

In spite of a large media coverage, the amount of microplastics in cosmetics (0.5%) is far from the main identified sources. However, with a total estimated microplastics emission in Germany of 330’000 t/a, this sector still accounts for 1’600 t/a of microplastics intentionally added to cosmetic products.

Particulates are mainly added to cosmetics as abrasives in exfoliation scrubs, handwash or toothpastes. Due to the lack of understanding of the influence of these additives on the ecosystem and human health, producers progressively remove or replace this component in their products. Furthermore, companies seek to stand out by completely banishing the use of non-biodegradable polymeric components in the formulation of their cosmetic products.[8]

Apart from abandoning particulate additives, the use of biodegradable microparticles offers a solution to the polluting effect of persistent plastics. Cellulose, sawdust, waxes and minerals belong to the list of possible alternatives. Replacement with biologically degradable polymers is a promising approach, which offers to use the existing process chain, since they exhibit very similar material properties compared to their synthetic non-biodegradable counterparts (thermal behavior, hardness, *etc.*).[9]

Polyhydroxyalkanoates (PHAs) belong to the class of biopolyesters. They are obtained from fermentation processes based on renewable resources as carbon substrates. Specific bacteria natively accumulate this thermoplastic polymer under defined growth conditions. It is stored intracellularly in so-called carbonosomes[10] with a diameter of 0.2–0.4 µm. The advantage of polyhydroxyalkanoates over other biopolymers is their excellent biodegradability. A study of the California Department of Resources Recycling and Recovery (CalRecycle) states that polyhydroxyalkanoates are degraded in a marine environment (38–45%) better than or as good as cellulose (38%). Samples of polylactide (PLA), another biopolyester used as an alternative in this context, was degraded to only 3% in the same experiment.[11]

At the Institute of Life Technologies, HES-SO Valais-Wallis in Sion, Switzerland, one of the focuses of the research group of Biotechnology and Sustainable Chemistry is the bacterial production of polyhydroxyalkanoates. Tailor-made polyhydroxyalkanoates (PHA) are developed for industrial and medical applications.[12–17] Several processing techniques are applied to the polyhydroxyalkanoate materials to eventually lead to micro-structured geometries or microparticles. Hereinafter we describe a selection of these methods to illustrate the versatility of this biopolymer.

2. Microporous Polymer Foams

One way to create a micro-structured biopolymer is to use salt leaching to generate open porous foams. Salt crystals of sodium chloride with a well-defined size act as porogens. The polymers are solubilized and the desired size fraction of sieved salt crystals is suspended homogeneously to a high weight content (90%) to ensure the open pore structure of the polymer foam. After evaporation of the solvent, the blend is suspended into water to dissolve the sodium chloride crystals leading to interconnecting voids (Fig. 1).

Potential applications of such porous materials are membranes,[18] scaffolds for tissue engineering,[19] and wound dressing.[20]

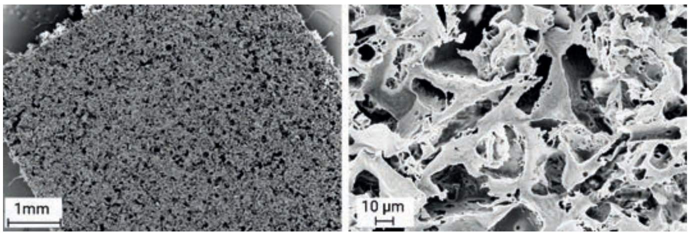

Fig. 1. SEM micrographs of open porous biopolymer foams with interconnecting voids obtained by salt leaching with 80–100 µm NaCl crystals suspended into a matrix of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) copolymer.

3. Micro- and Nanofibers

Electrospinning is a technique to produce micro- and nanofibers from melt or solvent solution. High voltage applied between the spinneret and the collector provides sufficient force to the droplet from the polymer feed to stretch it until a jet of liquid erupts from its deformed surface, the so-called Taylor cone.[21] The liquid jet dries in the electric field, while the charge migrates to the surface creating electrostatic repulsion of the produced fiber. This repulsion causes the fiber to further stretch and creates a well-defined and uniform diameter before it hits the grounded collector (Fig. 2). Electrospun fiber materials span a large field of possible applications. Filtration, wound dressing, fibrous drug delivery, fiber reinforcement of composite materials and support material for catalysts are only very few of a large number of examples.[22]

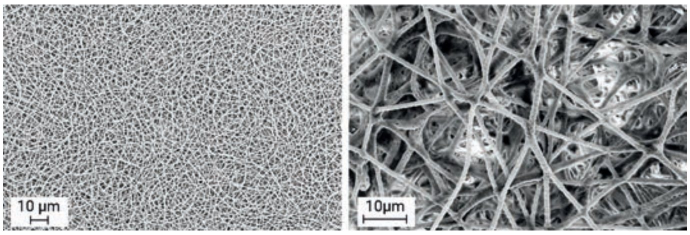

Fig. 2. SEM micrographs of electrospun microfibers of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) copolymer.

4. Micro- and Nanoparticles

With the same experimental setup as for the electrospinning of polymer solutions, particles can be produced by electrospraying.[23] When the electric repulsion in the electric field is high enough to overcome the molecular cohesion of the liquid in the jet, stream breakup occurs and droplets are formed, which further split into smaller droplets until they dry and finally reach the grounded collector in the form of micro- or nanoparticles (Fig. 3).

Micro- and nanoparticles can be used as fillers and additives and a lot of research focusses on the utilization of polyhydroxyalkanoates for the encapsulation of active pharmaceutical ingredients (APIs). Such API containing biopolyester particles can be deployed in controlled drug delivery.[24–26]

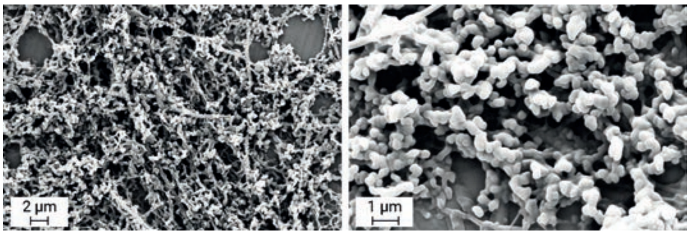

Fig. 3. SEM micrographs of nanoparticles obtained by electrospraying poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) copolymer.

5. Conclusions

Environmental pollution due to persistent plastic is a serious threat to today's ecosystems. Microplastics play an important role, since they are more difficult to be contained. They leak from purification or recycling systems (*i.e.* efflux from wastewater treatment plants) and it has been shown that airborne microplastics can contaminate the environment through atmospheric transport.[27] While avoiding the intentional use of primary microplastics in the first place offers a possibility to reduce the total emission, we believe that the use of non-persistent plastic can offer an effective alternative in many existing applications. Polyhydroxyalkanoates can be produced based on renewable carbon resources and are biodegradable in several environmental conditions. In contrast to other biodegradable polymers, bacterial degradation leads to the elimination of these polymers even in the marine environment. Their similarity to fossil-based thermoplastic polymers in terms of thermal and mechanical properties allows applying most of the existing processing techniques. Next to our activities on the improvement of the bacterial production and the tailoring of the biopolymer properties, we display in this article some of our results for the processing of these materials into micro- and nanometer geometries.

Received: August 12, 2019

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