

Microplastics and Cosmetics: A Historical Overview

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Abstract

For more than five decades, personal care and cosmetic products (PCCPs) have incorporated microplastics (MPs) into their formulations. Initially, naturally derived abrasives were employed; however, from the 1980s onward, synthetic plastic microbeads were increasingly adopted as polishing agents due to their lower cost, extended shelf life—particularly with respect to microbial stability—and reduced potential for skin irritation. Microplastics, especially those from rinse-off PCCPs, are subsequently released into the environment, raising significant environmental concerns. In response, regulatory measures have been introduced in several countries to restrict the use of MPs in PCCPs, prompting the development of alternative materials. This contribution examines the historical evolution of microplastic use in PCCPs, with particular emphasis on patent activity in this field.

Keywords

Microplastic, Nanoplastic, Microbead, Cosmetics, Personal Care and Cosmetic Product, Patent History

1. Introduction

Often, cosmetic and personal care formulations incorporate a wide variety of polymers, including natural polymers, synthetic organic polymers, and silicones [1]. These materials perform multiple functions, such as acting as film formers, emulsifiers, thickeners, texture modifiers, protective barriers, and aesthetic enhancers (Table 1). In particular, polymers are widely used as rheology modifiers in water-based formulations, which typically exhibit low viscosity.

To increase viscosity or form gels, formulators commonly rely on natural polymers such as polysaccharides, starches, xanthan gum, guar gum, carrageenan, al-

ginates, pectins, gelatin, and agar. Many of these natural polymers are chemically modified to improve their suitability for cosmetic applications, as exemplified by cellulose derivatives including hydroxyethylcellulose, methylcellulose, and hydroxypropylcellulose. In parallel, a range of synthetic polymers—such as polyacrylic acid and its derivatives (carbomers), polyacrylamides, and alkylene oxide-based homo- and copolymers—are frequently employed due to their functional versatility.

Also, in hair conditioning products, both natural and synthetic polymers are used to enhance texture, manageability, and performance. Natural polymers include hydrolyzed proteins, cellulose-based polysaccharides, and gums such as gum arabic and gum tragacanth, while commonly used synthetic polymers include polyvinylpyrrolidone, polyvinyl acetate, polyacrylates, polymethacrylates, polyvinylamides, polyurethanes, and silicones [2] [3].

Polyurethanes, in particular, are widely applied in both solvent-based and aqueous cosmetic systems. Solvent-based polyurethanes are frequently used as secondary film formers in nail products, whereas waterborne polyurethanes are commonly found in mascaras and skin care formulations [4].

Importantly, water-soluble functional polymers are polymers that dissolve completely in water to form true solutions. In cosmetic formulations, they are used to provide functions such as thickening, film formation, conditioning, or stabilization. Because they are dissolved at the molecular level, they do not exist as discrete solid particles and are not considered particulate matter in the environment. These polymers are not part of this review.

In contrast, a number of personal care and cosmetic product (PCCP) formulations contain solid, synthetic polymer particles in the micro- or submicron size range. They can be made of polyolefins (polythene, polypropylene and polyisopropylene), polystyrene, polyesters, polyamides (nylons), or similar polymers. These materials serve multiple functions, including acting as abrasives for exfoliation, smoothing, and polishing of the skin; as delivery systems for active ingredients; and as carriers of colorants. In addition, submicron polymer powders may be used for thickening, bulking, or modifying the sensory properties of products (Table 1). Due to their small size and solid polymeric nature, these materials are classified as plastics, specifically microplastics (MPs). In PCCPs, they are most commonly incorporated in the form of microbeads and as powdered material/particulate matter.

Table 1. A list of polymer types found in PCCPs along with their common uses/purpose (AACO = aromatic polyalkene co-polymer, APH= aromatic polyhydrocarbons), E = polyester, PA = polyalkene, ECO = ester co-polymer; PFA = polyfluoroalkene, Si = polysiloxane (silicone), U = polyurethane).

Item (polymer type)	Polymer	Common use/purpose in cosmetics
1 (A)	Nylon-6	Bulking agent, viscosity controlling
2 (A)	Nylon-12 (polyamide-12)	Bulking, viscosity controlling, opacifying (for example wrinkle creams)

Continued

3 (E)	Poly (ethylene terephthalate) (PET)	Adhesive, film formation, hair fixative; viscosity controlling, aesthetic agent, (for example glitters in bubble bath, makeup)
4 (E)	Poly (methyl methacrylate)	Sorbent for delivery of active ingredients
5 (E)	Poly (butyleneterephthalate)	Film formation, viscosity controlling
6 (E)	Poly (ethyleneisoterephthalate)	Bulking agent
7 (E)	Polyacrylate	Viscosity controlling
8 (E)	Acrylate copolymer	Binder, hair fixative, film formation, suspending agent
9 (E)	Allyl stearate/vinyl acetate copolymer	Film formation, hair fixative
10 (ECO)	Styrene acrylate copolymer	Application date
11 (PA)	Polyethylene (PE)	Abrasive, film forming, viscosity controlling, binder for powders
12 (PA)	Polypropylene (PP)	Bulking agent, viscosity increasing agent
13 (PFA)	Polytetrafluoroethylene (Teflon)	Bulking agent, slip modifier, binding agent, skin conditioner
14 (APH)	Polystyrene	Film formation
15 (AACO)	Ethylene/propylene/styrene copolymer	Viscosity controlling
16 (U)	Polyurethane	Film formation (for example facial masks, sunscreen, mascara)
17 (ECO)	Ethylene/methylacrylate copolymer	Film formation
18 (ECO)	Ethylene/acrylate copolymer	Film formation in waterproof sunscreen, gellant (for example lipstick, stick products, hand creams)
19 (AACO)	Butylene/ethylene/styrene copolymer	Viscosity controlling
20 (Si)	Trimethylsiloxysilicate (silicone resin)	Film formation (for example colour cosmetics, skin care, sun care)

Plastics are ubiquitous in modern society. The term “plastic” refers to polymeric materials that soften upon heating and can be molded into solid forms [5]. This category includes both virgin plastic pellets used in manufacturing and polymer resins blended with additives to enhance material performance [5]. Global plastic production has increased dramatically, rising from approximately 1.7 million metric tons in the early years of mass production during the 1940s and 1950s to 335, 400.4, 413.8, and 443.5 million metric tons in 2016, 2022, 2023, and the projected value for 2025, respectively [6]-[9]. This corresponds to an average annual growth rate of about 3.5% in recent decades. Plastic production is expected to reach approximately 1.12 billion metric tons by 2050 [10].

To date, an estimated 8,300 million metric tons of virgin plastic materials have been produced globally. By 2015, of the 6,300 million metric tons of plastic waste generated, only about 9% were recycled, 12% incinerated, and 79% accumulated in landfills or released into the natural environment [11] [12]. If current production

and waste management trends persist, plastic waste in landfills and the environment is projected to reach roughly 12,000 million metric tons by 2050 [11].

Once released into the environment, plastics persist for long periods of time. Most commonly used plastics are non-biodegradable and degrade primarily through abiotic processes such as through thermal oxidation [13], UV-driven photo-oxidation [14] [15], and hydrolysis [16], often combined with mechanical weathering [17]. These processes occur slowly, resulting in very long environmental half-lives [18]. The widespread and persistent presence of plastic debris has even been proposed as a geological marker of the Anthropocene epoch [19].

Plastics are commonly classified by particle size into macroplastics (> 10 mm), mesoplastics (5 - 10 mm), and microplastics (< 5 mm) [20]. The term “microplastics” was first introduced by Thompson *et al.* [21]. More recently, the term “nanoplastics” has been proposed, with some authors defining nanoplastics as particles ≤ 100 nm [22], while others suggest an upper boundary for nanoplastics of ≤ 1 μm [23] [24].

Microplastics and nanoplastics can originate from the fragmentation of larger plastic debris; however, they are also intentionally manufactured for specific applications. These intentionally produced particles are referred to as primary microplastics and nanoplastics [25] [26]. Major sources of primary microplastics include cosmetics [25], pharmaceuticals [27], textiles [28] [29], and sandblasting materials [30].

A substantial proportion of microplastics from these sources enters wastewater systems and is transported to wastewater treatment plants [31]. Although treatment plants retain a large fraction of microplastics in sewage sludge [32], some particles escape removal, leading to the classification of wastewater treatment plants as point sources of microplastic pollution in aquatic environments [33]. Additional sources include accidental spills of virgin plastic pellets during loading and off-loading operations and during maritime transport [34] [35].

Once in marine environments, microplastics can be ingested by aquatic organisms [36], some of which are subsequently consumed by humans as seafood [37] [38]. As a result, microplastics have now been detected in all major human organs [39]. While the potential health impacts of microplastics have long been suspected [40], recent studies have begun to establish clearer associations between microplastic exposure and specific health outcomes, including osteoporosis [41].

Although personal care and cosmetic products contribute a relatively small proportion of total plastic emissions—estimated at 0.1% - 4.1% depending on the study [28] [42] [43]—they represent a category of primary microplastics that can be effectively reduced through regulation. Plastic MBs used in PCCPs have therefore received particular attention. Their relevance is amplified by direct human exposure, including oral ingestion in products such as toothpaste [44]. Regulatory attention intensified with the U.S. Microbead-Free Waters Act of 2015 [45], which prohibited the manufacture and sale of rinse-off cosmetics containing plastic MBs. Other regions followed suit, as will be discussed below.

Historically, the most commonly used polymers in plastic MBs have included

polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), poly (methyl methacrylate) (PMMA), and nylon. However, not all MBs used in PCCPs are synthetic. Natural and biodegradable alternatives—such as cellulose, cornmeal, apricot kernels, walnut husks, and pumice—have been used throughout and are now widely employed as abrasives, bulking agents, opacifiers, and microbead substitutes [46]-[48]. **Table 2** presents a selection of natural materials either used concurrently to plastic microbeads/particulates or instead of these as abrasives/polishing agents in cosmetic formulations.

Table 2. Common natural abrasives used in cosmetics. (see also: [49])

Organism derived material	Secondary use	Inorganic natural material	Secondary use
Abalone shell powder	Binding, opacifying, and Bulking agent	Aluminum iron silicates (ceramic)	Bulking agent
Chitin	Bulking agent	Argilla (smectite mineral)	Bulking agent
<i>Cocos nucifera</i> (coconut) shell powder		Calcium titanium borosilicate	Bulking agent
<i>Helianthus annuus</i> (sunflower) seed powder	Absorbent	Fuller's earth (multani mitti)	
<i>Hordeum distichon</i> (barley) seed flour	Bulking agent	Hydrated silica	Bulking agent
<i>Juglans regia</i> (walnut powder)	Promotes cell turnover, reduces inflammation	Illite (clay mineral)	Adsorbent
<i>Linum usitatissimum</i> (linseed) seed flour	Bulking agent	Nephrite calcium magnesium silicate $\text{CaMg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$	
Nacre (mother of pearl) powder	Thickening agent	Pegmatite (igneous rock) can be made of quartz, mica and feldspar	Absorbent
<i>Oryza sativa</i> L. (Asian cultivated rice) germ powder	Bulking agent	Perlite (amorphous volcanic glass)	
<i>Phaseolus radiatus</i> seed starch	Bulking agent	Pumice (volcanic rock)	
<i>Prunus persica</i> (peach) seed powder	Absorbent	Salt (mostly NaCl)	Binding/thickening agent
<i>Simmondsia chinensis</i> (Jojoba) microbeads		Sodium/aluminum/iron hydroxide/oxalate/sulfate	Absorbent, opacifier
Wood powder	Thickening agent, binder	Titanium dioxide	
<i>Zea mays</i> cob meal	Binding agent	Volcanic ash (inorganic silicate obtained from lava deposits)	Absorbent

In the last decades, the percentage of MBs in the composition of PCCPs depended on whether the products were rinse-off or leave-off [50], where historically the percentage of MBs in the products differed widely and ranged from less than 1% to more than 90% [51]. It is important to note that MBs play a vital role in some of the cosmetics products. Their functions depend on their size, shape as well as composition [50]. While, as stated above, polymers in cosmetics are used as binders, bulking agents, emulsifiers, film formers, viscosity regulators, opacify-

ing agents, glitter additives, skin conditioners, tooth polishers in oral care, gellants in denture adhesives, moisturizers, UV filters, and stabilizers (see **Table 1** [52] [53]), only in some of the uses are the polymers used in form of actual plastic MBs. The focus of much of the literature is on the use of plastic MBs as exfoliants [54]-[56], especially in body and facial scrubs, shower gels and toothpastes. Oftentimes, here, the basic function of the MBs is to produce a smoother skin by increasing the rate of keratinization through exfoliation [57]-[59]. Abrasive scrubs can incorporate both natural and synthetic materials at the same time [60] to induce various degrees of exfoliation [61]. As we will see, the composition of abrasive material in PCCPs has changed over time, beginning with exclusively natural material, then, with the advent of synthetic polymers incorporating plastic MPs and currently experiencing a policy driven phase out of such plastic MBs. This contribution aims to outline the historical development of microplastic-containing PCCPs, including an examination of patent trends over time, and to trace the gradual elimination of these materials from such products in light of the evolving understanding of the potential human health impacts of microplastics from cosmetics. In addition, the article explores the search for alternative materials to replace MBs in cosmetic formulations.

2. Methodology

To date, a number of reviews on different aspects of MPs in cosmetics have appeared in form of journal articles [52] [56] [62]-[69] and of book chapters [70]-[72] including on new developments in biodegradable MBs [52] [73] [74] and on health implications of MPs in cosmetics [68] [69] [72]. For the current review, the databases Scopus®, SciFinder® and Web of Science® as well as the search engines google search® and google scholar® were utilized. Key word combinations such as “microplastics AND cosmetics”, “microbeads AND cosmetics”, “microplastics AND toothpastes”, “microbeads AND toothpastes”, “microplastics AND personal care products”, “microbeads AND personal care products” were used in the searches. For exclusion/inclusion of the articles, first the titles and then the abstracts of the respective papers were evaluated. References cited by the chosen articles were scrutinized as to their relevancy as were all the manuscripts that were listed in the citation index of the chosen articles. For the patent search, keyword combinations such as “polythene/polyethylene AND cosmetics” and “plastic AND cosmetics” were used, covering the period from 1959 to the present. The database SciFinder® was used to search for patents published on MPs in PCCPs. Patents were viewed through PatentPak® as embedded in SciFinder®. Furthermore, copies of some of the patents were obtained through the search engine google patents® (<https://patents.google.com>), through Espacenet® (<https://worldwide.espacenet.com/patent/>) as well as through Justia® patents (<https://patents.justia.com/>). Also, the webpage <https://www.epo.org/en/searching-for-patents/technical/publication-server> was used to receive access to copies of European patents. Journal articles were mostly acquired through the UAEU electronic library. In the review, the collection of pa-

tents on plastic microbeads and microspheres and their substitutes in cosmetic formulations is intended to be illustrative and is not exhaustive. Thus, while some of the patents are seminal in the field, other patents are chosen to be representative of a larger body of similar patents.

Various polymers used in cosmetics are either water-soluble or incorporated in emulsions without forming solid microplastics (MPs). Although reference is given to them, these types of polymers are largely excluded from the scope of this review. Additionally, the review does not address inadvertently added MPs, such as those resulting from the degradation of cosmetic plastic packaging—e.g., MPs generated when opening the plastic lid [75] to a packaged PCCP. It also does not cover MPs formed during the manufacturing or recycling processes of such packaging, although these have become a focus of emerging government regulations [76]-[79].

3. The Beginnings

Facial cosmetics have been a part of human culture for millennia, and recent studies suggest that *Homo sapiens* may not be the only humanoid species to have used body ornamentation. Evidence indicates that even Neanderthals (*Homo sapiens neanderthalensis*) might have utilized mineral-based pigments, such as hematite (Fe_2O_3), goethite [$\alpha\text{-Fe(O)OH}$], and pyrite (FeS_2), for decorative or ritual purposes [80].

In more recent history, the use of cosmetics is well-documented, not only through archaeological discoveries but also in written texts. One notable example is the Roman poet Ovid (43 BC - 17 AD), who composed a poem titled *Medicamina faciei femineae*, which includes four complete recipes and one fragmentary recipe for topical facial applications [81]. These ancient formulations, much like today's facial cleansers, featured a balance of liquid or oily bases with solid ingredients—both organic and inorganic. These solids performed functions similar to those of modern facial products, such as exfoliation and cleansing. Notable ingredients in Ovid's recipes included salts like Libyan Desert salt (*sal ammoniacum*), natron, and red natron (sodium carbonate hydrate with cyanobacteria such as *Spirulina*, giving it a reddish hue). Also included were ground oyster shells, chalk dust, and Melos clay [81] [82]. Organic abrasives like ground charcoal, deer antlers, and spelt (Dinkel wheat) were also used. The intended effects of these formulations were to remove makeup, lighten the skin, smooth the complexion, and conceal blemishes—goals that remain central to modern cosmetic products.

Alongside these early cleansers, the use of pigments in facial cosmetics became more diversified. The black pigment kohl, traditionally made from ground stibnite (Sb_2S_3), and the brilliant red vermilion made from ground cinnabar (HgS) were widely used. Other pigments, such as red lead tetroxide (Pb_3O_4) and white ceruse ($2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$), were common in certain social circles from the Renaissance through the 18th century. By the 19th century, zinc oxide began replacing white ceruse as the preferred face powder. Organic dyes were also used, with substances like alkanet (from *Alkanna tinctoria*) and the red-orange dye from safflower (*Carthamus tinctorius*) being favored. In the section below, we will see that for many

years from the late 1970s to the 2020s the colors of many body scrubs, body shampoos and toothpastes were imparted by colored MBs, where metal phthalocyanins such as phthalocyanins green and blue, triphenylmethane dyes such as brilliant blue FCF, or azo-organic substances such as pigment red 5 were often involved.

Turning back to the development of abrasive agents in personal care products, it is important to consider the composition of soaps and scrubs from the late 19th and early 20th centuries (Table 3). During this period, patenting new product formulations became increasingly common. Abrasive agents added to cosmetic soaps were often sourced from natural materials. These included china clay, bentonite [83], calcined diatomaceous earth [84], Fuller's earth [85], tripoli [86], volcanic ash [87], feldspar [87], powdered pumice, bath bricks [88], amorphous silica [89], cornmeal [90], sawdust [91] [92], ground wood [91], and cork [91]. By 1938, reviews on soap compositions, including on abrasive components, began to emerge [93], and in 1939, a comprehensive review of abrasives in soaps and scouring powders was published [94].

Table 3. Patents on new detergents, cosmetic soaps and toothpastes utilizing inorganic salts and organic natural products as abrasives/polishing agents.

Inventor	Assignee	Country of application	Application date	Granted date	Patent number	Description
C.J. Munter [95]	Hall Labs LLC	United States	June 1 st , 1945	Jan. 17 th , 1950	US 2494827A	Abrasive detergent compositions: the abrasive effect of slowly dissolved metaphosphates is named. Other named abrasives are silica and corn meal
F.C. Atkinson [96]	American Hominy Corp	United States	April 4 th , 1919	May 15 th , 1923	US 1455015A	Cellulose obtained from corncobs as semiabrasive material
G.M. Salzmann and R.J. Schiraldi [97]	Colgate Palmolive Corp.	United States	July 18 th , 1952	May 1 st , 1956	US 2744049A	Stabilized dental creams using calcium salts as abrasives
F.E. Lauster [98]	Cameo Inc.	United States	Sept. 7 th , 1969	Aug. 8 th , 1972	US 3683065A	Liquid dentrifice using CaHPO ₄ ·2H ₂ O as polishing agent

Some drawbacks were noted regarding the use of certain abrasive materials in cosmetics, including challenges related to sourcing and shelf life, especially concerning microbial growth. Additionally, it was observed that some abrasives, particularly those found in toothpastes, could cause microinjuries to the skin, teeth, and mucous membranes [99]. In fact, F.E. Lauster in patent US3683065A [98] on liquid dentrifice clearly distinguishes between, abrasion/abrasive' and "polishing agent", which indicates that abrading was seen to have some connotation close to mechanically damaging tooth enamel. In the patent, dicalcium phosphate dihy-

drate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) is seen as a possible polishing agent.

Table 4. Early patents which specify the development, formulation and production of plastic microspheres for cosmetic use.

Inventor	Assignee	Country of application	Application date	Granted date	Patent number	Description
M. Blaustein [100]	Phillips Petroleum Corp.	United States	Oct 5 th , 1959	July 20 th , 1965	US 3,196,079	Cosmetic powder compositions containing a finely divided, high density polyolefin as a substitute for talc
R.L. Smith <i>et al.</i> [101]	Permutit Co Ltd.	UK	April 6 th , 1967	Nov. 6 th , 1969	GB 1169323	Co-polymer microbeads for cosmetic usage
R.L. Smith and G. Woodford [102]	Permutit Co Ltd.	UK	Feb. 7 th , 1966	Feb. 5 th , 1969	GB 1141994	Crosslinked vinyl polymer microbeads in cosmetic powders
R.L. Smith [103]	Permutit Co Ltd.	UK	Jan. 22 nd , 1968	Sept. 23 rd , 1970	GB 1205883	Lipsticks containing crosslinked vinyl copolymer microbeads
C. Picker and P. Schaefer [104]	Individual	Germany	May 12 th , 1975	March 24 th , 1977	DE 2521003B1	Hollow air-filled microspheres of vinylidene chloride copolymers for cosmetic creams and salves
K. Oka [105]	Toray Ind. Inc.	USA	Sept. 17 th , 1984	May 13 th , 1986	US4588617A	Process for producing cured epoxy resin spherical particles for use in cosmetics
S. Kato [106]	Techol Riso-Oshizu-Inko-Oporee-Tetsudo KK	Japan	May 27 th , 1985	Dec. 1 st , 1986 (publication)	JP 61271330 A	Preparation of thermoplastic microbeads
K. Oka <i>et al.</i> [107]	Toray Ind. Inc.	Japan	Oct. 31 st , 1986	May 18 th , 1988 (publication)	JPS63113024A	Colored high polymer fine particle
Y. Kaneda <i>et al.</i> [108]	Pola Orbis Holdings Inc.	Japan	Oct. 2 nd , 1984	April 30 th , 1986 (publication)	JPS6185309A	Solid powder cosmetic with nylon microparticles

Table 5. Patents on formulations of cosmetics, detergents and scouring liquids that contain solid polymeric microbeads/powder as abrasives/polishing agents and for coloration, spanning five and a half decades.

Inventor	Assignee	Country of application	Application date	Granted date	Patent number	Description
D.J. Guest and W.I. Williamson [109]	ICI, Ltd.	United States	Jan 31 st , 1964	June 20 th , 1967	US 3,326,807A	An opaque liquid detergent composition containing essentially a liquid synthetic detergent and an aqueous dispersion of a copolymer of styrene with at least one ethylenically unsaturated monomer such as acrylamide

Continued

G. Bell, Jr. [110]	Avisun, Corp.	USA	Aug. 10 th , 1965	May 14 th , 1968	US 3,383,320A	Detergent bar having a solid watersoluble detergent held in a solid matrix of a sintered thermoplastic resin wherein the resin can be polypropylene, propylene-ethylene copolymer or polyethylene
W.J. Beach [111]	Sugar Beet Products Corp.	USA	July 27 th , 1967	Feb. 29 th , 1972	US 3,645,904	Skin cleaner which eliminates mineral-based abrasives such as aluminum oxide, volcanic ash, and the like and substitutes therefor a resilient plastic such as polyethylene
D.N. Vincent [112]	Champion International Corp	USA	June 3 rd , 1974	Dec. 30 th , 1975	US 3930101A	Inorganic pigment loaded polymeric microcapsular system, e.g., made of polystyrene
F.E. Chapman [113]	S.C. Johnson & Son, Inc.	USA	Nov. 29 th , 1978	Dec. 23 rd , 1980	US 4,240,919A	Thixotropic abrasive liquid scouring composition—as possible abrasive ground rigid polymeric materials are mentioned
J.S. Kanfer <i>et al.</i> [114]	Go-jo Industries	USA	March 26 th , 1987	Nov. 22 nd , 1988	US 4,786,369A	Integral dry abrasive soap powders. Rigid polymeric or synthetic plastics materials such as polyethylene, melamine, urea formaldehyde resins, and polyurethane foam are mentioned as abrasives
G. Van Puyvelde [115]	Maclean S.A.	Luxemburg	Dec 21 st , 2001	June 25 th , 2003	EP 1321514A1	Liquid detergents containing polyethylene particles for scouring hard surface
H. Albrecht <i>et al.</i> [116]	Beiersdorf AG	Germany	Aug 13 th , 2002	March 4 th , 2004	DE 10237008A1 (withdrawn)	Cleansing compositions for cosmetic and house-hold purposes containing abrasives, hydrocolloids and surfactants
T. Horibata <i>et al.</i> [117]	Kao Corp.	Japan	Dec. 3 rd , 2012	Jan 18 th , 2017	JP 6063725B2	Pigment granules consisting of polyvinyl pyrrolidone and <u>acid-modified</u> polyvinyl alcohol

Continued

N. Wakabayashi [118]	Tokiwa Corp.	Japan	Oct 16 th , 2019	May 22 th , 2020	WO 2020100510A 1	Solid powder cosmetic containing sili-cone wax and poly-ethylene terephthalate powder
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The introduction in the second half of the 20th century of synthetic polymer MBs as uniform and controllable exfoliants occurred against this backdrop (**Tables 4-5**). They were seen as mild abrasives and polishing agents with predictable textures, particle sizes, and exfoliation efficiency that came at a competitive cost. Early patents of synthetic MBs in personal care products began in the 1960s, with the first relevant patent in regard to plastic MBs granted in July 1965 [100], but they were not regularly included commercially until the 1990s, when they were considered a go-to source of innovation in personal care products. In 1972, MBs were patented for their current use in cosmetics as cleaning or exfoliating agents [111], and were only seen infrequently until the early 1990s [119], when cosmetic manufacturers started substituting synthetic polymeric beads for the most common inorganic peeling ingredients of the time, such as aluminum oxide [42], or other natural materials like millet or pumice peels [120]. MBs had become so common by the early 2000s that it was estimated that every household used at least one microbead scrub on a regular or weekly basis [54]. With the article by Zitko and Hanlin in 1991 [119], academia and the general public were made aware of the polluting potential of microplastics from rinse-off cosmetics. It was not until 2015, with the passage of the Microbead-Free Waters Act [45] by the U.S. Congress in 2015-2016, that a major country enacted binding legislation to restrict the use of plastic microbeads in rinse-off PCCPs. Consequently, the majority of plastic microbead use in rinse-off PCCPs occurred between approximately 1991 and the point at which meaningful legislation was introduced in a given region.

4. Plastic Microbeads in Commercial Cosmetic Formulations

The first patents on the use of plastic microbeads/plastic microparticles in PCCPs, especially in body scrubs and other rinse-off cosmetics, made use of polyolefins as materials [100], specifically polythene and polypropylene. Examples of synthetic solid particles used in PCCP formulations include nylon, silicone resin, poly(meth)acrylate, polyethylene, polyester, polypropylene, polystyrene, polyurethane, polyamide, epoxy resin, urea resin, and acrylic powder (**Table 6**). Non-limiting examples of useful solid particles include Microease 110S, 114S, 116 (micronized synthetic wax), Micropoly 210, 250S (micronized polyethylene), Microslip (micronized polytetrafluoroethylene) and Microsilk (a combination of polyethylene and polytetrafluoroethylene), all of which are available from Micro Powder, Inc. Other examples include MP-2200, BPA-500 (polymethylmethac-

rylate), EA-209 (ethylene/acrylate copolymer), SP-501 (nylon-12) available from KOBO Products Inc., e.g., via Equistar, SP-10 (nylon-12), ES-830 (polymethylmethacrylate), BPD-800, BPD-500, BPA-500 (polyurethane) and CL2080 (polyethylene) particles, obtained from Quantum Chemical. Spherical polyethylene is also sold under the trade name Microthene, including MN701, MN710, MN-714, MN-722 and FN5100 (Table 7). Nylon particles are available from Elf Atochem under the trade name Orgasol. Advanced Polymer Systems (Advanced Examples include Microsponge and Polytrap acrylate copolymers available from Polymer Systems, and the Tospearl particle silicone resin sold by GE Silicones. Also useful is Ganzpearl GS-0605 cross-linked polystyrene (available from Preperse).

A search in google patents[®] with the keywords, microthene' and, cosmetics' delivered 1262 results. Although the authors did not examine all 1,262 patents individually, a review of the first 100 results clearly showed that the vast majority (90%) referred to Microthene™ FN510-00 (Equistar), Microthene™ MN 727 or Microthene™ MN 710-20, all being polythene MBs. It should be noted, however, that in most patented formulations for personal care products (Table 6), a wide range of options is typically specified for the solid particles, encompassing natural, semi-synthetic, and fully synthetic materials. These include patents applied for in the first decade of the 21st century. Patents by Gonzalez *et al.* [121], Tanner and Manohar [122], and Osborne [123] illustrate this point. Even in the second decade of the 21st century polythene was included in some patents—these pertained to solid, leave-on cosmetics. It should also be noted that the above named commercially available plastic MBs/plastic microparticles are marketed for a whole range of purposes and have other uses such as binders in filters and battery materials or as carriers/matrices in fabrics or paper (Table 7).

Table 6. Patents on formulations of cosmetics, incl. toothpastes, with visible solid plastic microbeads and/or solid microbeads containing synthetic polymers as cleansing/polishing agents.

Inventor	Assignee	Country of application	Application date	Granted date	Patent number	Description
Warner Lambert Co LLC [124]	Warner Lambert Co LLC.	France	Oct 30 th , 1973	July 28 th , 1978	FR 2204400B1	Water-wettable anhydrous products, such as the powders and creams used in cosmetic are admixed with 20 - 60w% PE or PP
G. Mannara [125]	Colgate Palmolive Co	USA	Oct. 20 th , 1976	Jan. 17 th , 1978	US 4069312A	Dentifrice speckles of substantially uniform shape and size that can be made among other materials of PE or PP

Continued

M. Bares <i>et al.</i> [126]	Vs Chemicko-Technologicka	Belgium	Nov 19, 1981	Mar 16, 1982	BE 891188A1	The fragrance of perfumes—particularly volatile components used to scent soaps and detergents—is to be stabilized by immobilizing the perfume molecules within polymers such as polystyrene, acrylonitrile-butadiene-styrene (ABS) copolymers, vinyl acetatevinyl chloride copolymers, and poly (vinyl acetate)
T. Murata <i>et al.</i> [127]	Shiseido, Co., Ltd.	Japan	Feb. 6 th , 1985	Aug. 13 th , 1986 (published)	JPS 61180707A	A solid powdery cosmetic, consisting of 60 - 90 wt% powder, (powder usually usable in makeup cosmetic, particularly polyethylene powder
P. Bottiglieri [128]	Givenchy Parfums	Switzerland	May 23 rd , 1989	Sept. 30 th , 1991	CH 678488A5	Cosmetic exfoliant composition with polyethylene beads of controlled size as abrasive
M.S. Wdowik [129]	Edgewell Personal Care Brands LLC	USA	April 18 th , 1996	Dec. 24 th , 1996	US 5,587,156A	Shaving compositions that include solid particulate additives which provide improved razor blade glide. Additives can include polyamides (nylon), PE, PP, and polyfluoroethylene
C.H. Suhonen [130]	Alticor Inc.	WIPO	Feb. 14 th , 2001	Aug. 16 th , 2001	WO 2001058416A2	Toothpastes that include wax microbeads with PTFE incorporated in them
R. Miyake and Y. Masubuchi [131]	Kose Corp.	Japan	Dec. 1 st , 2015	Dec. 2 nd , 2020	JP 2016113446A	A solid powder cosmetic comprising 3 to 40% by mass of a spherical polyolefin (eg., PE) resin powder having an average particle diameter of 1 to 50 μm

*HDI = Hexamethylene diisocyanate.

Table 7. Typical plastic microsphere products used in cosmetics over the years. There are many other uses for the products as in packaging, agriculture, healthcare, and industrial products. Typical examples are the use as binders in filters and battery materials or as carriers/matrices in fabrics or paper.

Product name	Polymer type	Size range	Density	Melting point	Shape
SP-10 (KOBO-Products)	Nylon-12	8 - 12 μm	0.2 - 0.45 g/cm^3 (bulk density) 1.01 - 1.02 g/cm^3 (true density)	178 - 180 °C	Spherical
SP-501 (KOBO-Products)	Nylon-12	5 - 10 μm	0.2 - 0.45 g/cm^3 (bulk density) 1.01 - 1.02 g/cm^3 (true density)	178 - 180 °C	Spherical
BPD-500 (KOBO-Products)	HDI*/trimethylol hexyllactone crosspolymer (and) silica	15 μm	0.55 g/cm^3 (bulk density)		Spherical
BPD-800 (KOBO-Products)	HDI*/trimethylol hexyllactone crosspolymer (and) silica (3.0 - 5.0%)	5.5 - 10.2 μm	0.37 g/cm^3 (bulk density)	NA	Spherical
Micropoly 210 (Micro Powders, Inc.)	Polythene	15 - 20 μm	~0.92 g/cm^3	~109 - 112 °C	Spherical
Micropoly 250S (Micro Powders, Inc.)	Polythene	2.0 - 4.0 μm	0.97 g/cm^3	129 - 131 °C	Spherical
BPA-500 (KOBO-Products)	Polymethyl methacrylate (PMMA)	9 μm	1.18 g/cm^3	Glass transition temp. ~105 °C	Spherical
Microslip 519 (Micro Powders, Inc.)	PTFE	NA	NA	NA	NA
MN701 (Microthene)	Polythene	500 μm (35 mesh)	0.912 g/cm^3	100.8 °C/	Irregular
MN71020 (Microthene)	Low density polythene	292 μm (50 mesh)	0.915 g/cm^3	102.7 °C	Irregular
MN-71400 (Microthene)	Low-density polythene	292 μm (50 mesh)	0.913 g/cm^3	100.8 °C	Irregular
MN-72200 (Microthene)	Low-density polythene	292 μm (50 mesh)	0.923 g/cm^3	109.0 °C	Irregular
FN5100 (Microthene)	Low-density polythene	20 μm (5 - 50 μm)	0.923 g/cm^3	110.0 °C	Spherical
CL2080 (Quantum chemical spherical)	Low-density polythene	~8.0 - 14.0 μm	NA	110.0 °C	Spherical

The first influential study to examine plastic microbeads in PCCPs, while also emphasizing their potential as environmental pollutants, originated in Canada, in which Zitko and Hanlon [119] analyzed two skin cleaners. One contained a small concentration of MPs of undefined composition, while the other had an appreciable concentration of polystyrene beads. New Zealand [119]. Both of the next studies

originate from New Zealand, where Gregory [132] found MPs in 3 hand cleaners and in 3 facial scrubs and Fendall and Sewell [54] identified plastic microbeads in four PCCPs (Table 8). In 2015, Chang published a study examining nine branded PCCPs that were selected from a larger pool based on the presence of polyethylene listed in their ingredient list [60] [133]. In the same year, Napper *et al.* [25] published their results on six PCCPs sourced in Plymouth, UK, which were again selected as they had listed PE as an ingredient. In 2017, Cheung and Fok [134] looked at 9 popular PCCPs used in Hong Kong SAR and found that all 9 possessed PE/LDPE MBs. Two other studies on the presence of plastic MBs in PCCPs were published in 2017, one from China [135] and the other from Slovenia [136]. In 2018, Praveena *et al.* [137] studied 5 facial scrubs and 5 tooth paste products commercially available in Malaysia. Here, all facial scrubs contained either PE or PP microbeads, while the microbeads of only one toothpaste brand were made of PE.

The Microbeads free water act of 2015 instituted a sales ban in USA of plastic MB containing rinse-off PCCPs from January 2018 onwards, and this would be expected to have had a substantial impact on the production and distribution of U.S.-manufactured products, including their export to global markets, which also includes at the time existing stocks, as well as on the formulation and distribution of international products beyond the United States. Two notable studies published in 2019 merit attention, as this year represents a transitional period in the regulation of microplastic-containing microbeads, while acknowledging that the findings reported in 2019 are based on research conducted in preceding years. Godoy *et al.* [138] published an extensive investigation of PCCPs acquired in Granada, Spain, encompassing over 1500 products, including 68 scrubs. Although PE microbeads were present in 42.6% of the scrub products, their overall occurrence across all products analyzed was relatively low, at 1.82%. Ustabasi and Baysal [139] studied the compositions of 20 toothpastes bought in Istanbul, Turkey, where 20% of the samples were found to contain PE MPS at concentrations between 0.4 and 1 w%.

In the years after, numerous studies investigating the presence of plastic microbeads in PCCPs have been conducted across different regions and time periods. This temporal and geographic variation is important to consider, as regulatory frameworks governing the use of plastic microbeads in rinse-off cosmetics have differed between regions and over time, and continue to do so today, as outlined below. Indeed, presently some countries have implemented outright bans on rinse-off cosmetic products containing plastic microbeads, resulting in the removal of such products from the market and the imposition of fines on non-compliant companies. In other regions, stringent restrictions on microplastic-containing cosmetics are imminent, and only a limited number of rinse-off PCCPs containing microplastics remain available; however, enforcement mechanisms, such as active market surveillance, are often lacking. Finally, there are countries where no specific legislation addressing microplastic-containing rinse-off PCCPs exists, or where proposed regulations have not yet been enacted. In many instances, these

measures are introduced not as stand-alone regulations but as part of broader initiatives aimed at reducing or banning single-use plastics more generally. Implementation is frequently delayed, sometimes for several years. These latter jurisdictions are often of particular interest when assessing the range of PCCPs available on the market. Accordingly, during our investigation of microbead-containing rinse-off cosmetics and toothpastes in the United Arab Emirates between 2018 and 2022—a period in which the UAE did not yet have comprehensive legislation addressing single-use plastics—it was noteworthy that the availability of products containing plastic MBs declined over time [140] [141]. Nearly all rinse-off products manufactured in the UAE were free of plastic MBs and instead contained natural exfoliating materials, such as ground walnut shells. Products that continued to contain plastic MBs were, interestingly, imported by companies based in East Asia, Europe, or the United States. With respect to toothpastes, no products containing plastic MBs were identified in UAE supermarkets [142]. This includes products directly imported from Syria. The authors also obtained products through online retail platforms. Here, interestingly only toothpastes that predated the implementation date of the US Microbeads free water act of 2015 were found to have plastic MBs.

A number of recent studies from South Asia, particularly from India, Pakistan, and Sri Lanka, indicate that a substantial proportion of PCCPs still contain plastic microbeads. Thus, Gamage and Mahagamage [143] analyzed 15 personal care products available in Sri Lanka, including face washes, facial scrubs, baby creams, shaving creams, and skin creams, and identified microplastics in only six brands. The detected particles were predominantly white and consisted mainly of low-density polyethylene and ethylene-propylene copolymers, with particle sizes ranging from 238.55 ± 50.74 to 450.69 ± 174.9 μm . For identification, the study used the dyeing of the particles with Nile red and FT-IR spectroscopy. In Punjab, Pakistan, Hussain *et al.* [144] have studied 103 body scrubs and face washes from different markets in Jhang, Multan, and Bahawalpur and found that 47 (45.6%) products incorporated plastic microbeads, including 44 (42.7%) products that exhibited polythene microbeads. A smaller number of rinse-off cosmetics was scrutinized by Bhasvar and Gore [145] where three out of the analyzed six PCCPs contained polyethylene (PE) beads. Madhumitha *et al.* [146] found MPs in all the ten tooth pastes investigated, which were acquired in Tamil Nadu markets.

Further studies come from East and South East Asia. In 2021, Bashir *et al.* [147] looked at 144 PCCPs that were bought in Macao, China. Of the 68 facial cosmetic products analyzed, 44 (64.7%) contained microplastics in their formulations; specifically, polyethylene was detected in 43 products, polyethylene terephthalate in three products, and nylon in one product. Among the 31 body cosmetic products examined, 9 (29.0%) contained polyethylene microplastics. In addition, all 45 of the remaining cosmetic products analyzed contained microplastics, including 24 with polyethylene (PE), 3 with polyethylene terephthalate (PET), 12 with polymethyl methacrylate (PMMA), and 14 with nylon. The three top-sale products con-

taining microplastics were found to have particles of the size range of 11 to 968 μm . The MP concentrations were 7,674, - 18,216 P/g product with a weight percentage of 1.8 - 5.2%. In Selangor, Malaysia, Suardy *et al.* [148] found that all of the 6 investigated products contained MPs, 4 of them PE and 2 polystyrene (PS). Dung *et al.* [149] reported on the composition of 9 PCCPs from Ho Chi Minh City, finding MBs in all of them. In regard to the composition of the MBs, Dung *et al.* rely mostly on the ingredients lists. Only 2 of the 9 products contain PE MBs.

In the time period 2020-2023, three important studies originated from Eastern Europe. In Romania, Banica *et al.* [150] found MPs in all 5 PCCPs analyzed, which included body sprays and shower gels. In a 2020 publication, Piotrowska *et al.* [151] reported that, among 130 randomly selected scrub-type cosmetic products from 74 different manufacturers, 58 products (44.6%) contained natural abrasives, while 50 products (38.5%) contained polyethylene microparticles. Twenty-two cosmetics (19.9%) included both polyethylene and abrasives of natural origin. Three year later, in 2023, Guzik *et al.* [152] published that she and her team had isolated MPs from 13 of 50 randomly selected rinse-off products. Here, however, PE was not present in any of the products; instead, the formulations contained acrylate/C10-C30 alkyl acrylate crosspolymers, polystyrene-acrylate copolymers, and polylactic acid [152].

Two further, recent investigations come from Iran and Russia. Nasrabadi *et al.* [153] found that all the 6 PCCPs they chose from markets in Iran carried microplastics, mostly PE. 4 of 8 PCCPs from Russian markets as analyzed by Zorin *et al.* [154] carried MPs.

In all, it must be realized that many of the early investigations of PCCPs specifically looked at cosmetics with MPs to measure their concentrations, compositions and sizes [54] [60] [119] [132] [133]. Only a limited number of published academic studies [135] [138] [140]-[143] [147] [151] [152] have examined a sufficiently large sample of cosmetic products to provide a robust assessment of microplastic prevalence in the marketplace. Nevertheless, the available studies suggest that within the European community [136] [151], the number of PCCPs with intentionally added microplastics has declined markedly. Similar reductions have also been observed in certain regions, such as parts of the Middle East, where the prevalence of microplastic-containing PCCPs has decreased significantly [140]-[142], although no specific legal restrictions are in place, yet. Data from South Asia suggests that MP containing PCCPs are still on the market [142] [143] [145] [146]. Recent academic studies on the prevalence of MPs in PCCPs from North America, the European community and Japan are scarce.

Table 8. Published studies of MP content in PCCPs in different countries.

Reference	Total number of used products	MP containing products	MP/g in MP containing products	MP size	Country
Zitko and Hanlon (1991) [119]	2 (skin cleaners)	2	467 mg MP/g product		Canada

Continued

Gregory (1996) [132]	6 (3 hand cleaners, 3 facial scrubs)	6	Facial scrubs: 1.62 - 3.04 w% Hand cleaners: 0.19 - 6.91 w%		New Zealand
Fendall and Sewell (2009) [54]	4	4(100%)		4 - 1240 μm median range: 197 - 375 μm	New Zealand
Chang (2013, 2015) [60] [133]	9	9	0.08 - 0.1 g MB/mL product	183 \pm 58 μm - 317 \pm 110 μm (2015) 60 - 800 μm	USA
Napper <i>et al.</i> , (2015) [25]	6	6	919 - 18,906 P/mL product	164 - 327 μm	UK
Cheung and Fok (2017) [134]	9 body scrubs	9 (100%)	5,219 - 50,391 P/g product	85 - 186 μm	Hong Kong SAR
Lei <i>et al.</i> (2017) [135]	126 facial cleaners/16 brands	9 (7.1%)	25.0 \pm 10.7 mg MP/g product	200 - 380 μm	PR China
Lei <i>et al.</i> (2017) [135]	135 tooth pastes/23 brands	0%	-	-	PR China
Lei <i>et al.</i> (2017) [135]	136 shower gels/30 brands	3 (2.2%)	17.8 \pm 7.5 mg MP/g	341 - 468 μm	PR China
Kalčíková <i>et al.</i> (2017) [136]	5	4 (80%)	0.42 - 11.2 mg MP/mL	37.7 - 75.0 μm	Slovenia
Praveena <i>et al.</i> (2018) [137]	5 body scrubs	5 (100%, PE and PP)	11,776 - 36,636 MP/g		Malaysia
Praveena <i>et al.</i> (2018) [137]	5 tooth pastes	1 (20%)	48,992 \pm 1396 MP/g (all particle types)		Malaysia
Godoy <i>et al.</i> (2019) [138]	315 body products (19 body scrubs)	12 (3.81%) 63.2% of scrubs	up to 7.8 w%	5 - 2188 μm	Spain
Godoy <i>et al.</i> (2019) [138]	786 facial products (40 facial scrubs)	11 (1.40%) 27.5% of scrubs	1.9 - 5.6 w%	8.7 - 2188 μm	Spain
Godoy <i>et al.</i> (2019) [138]	44 foot products (5 foot scrubs)	4 (9.09%) 80% of scrubs			Spain
Godoy <i>et al.</i> (2019) [138]	469 bath gels (4 scrubs)	2 (0.43%) 50% of scrubs	1.0 - 1.3 w%	15 - 1260 μm	Spain
Ustabasi and Baysal (2019) [139]	20 tooth pastes	4 (20%)	0.4 - 1 w%		Turkey
Habib <i>et al.</i> (2020) [140]	37 body scrubs	Year 2018: 11 (29.7%)	131 - 12,412 MP/g product	35.9 - 115.8 μm	UAE

Continued

Piotrowska <i>et al.</i> (2020) [151]	130 body scrubs	80 (61.5%)			Poland
Bashir <i>et al.</i> (2021) [147]	68 facial skin care products	64.7% (63% PE)			Macao, PR China
Bashir <i>et al.</i> (2021) [147]	31 body skin care products	29% PE			Macao, PR China
Bashir <i>et al.</i> (2021) [147]	45 cosmetic products	100% (53.3% PE)			Macao, PR China
Suardy <i>et al.</i> (2020) [148]	6	6 (100%)		98-300 µm	Selangor, Malaysia
Habib <i>et al.</i> (2022) [141]	89 body scrubs	Year 2019: 11(12%)			UAE
Habib <i>et al.</i> (2022) [141]	74 body scrubs	Year 2020: (9, 12%)			UAE
Elkashlan <i>et al.</i> (2022) [142]	33 tooth pastes	0%	-	-	UAE
Madhumitha <i>et al.</i> (2022) [146]	10 tooth pastes	100%			India
Bhasvar and Gore (2023) [145]	6	3			India
Banica <i>et al.</i> (2023) [150]	5	100% (MBs of unclear composition)			Romania
Guzik (2023) [152]	50 abrasive cosmetics	13 (26%)			Poland
Gamage <i>et al.</i> , (2024) [142]	15	6	0.2 - 3.36	301 - 451 µm	Sri Lanka
Dung <i>et al.</i> (2024) [149]	9	9 (PE:2 [22.2%])	236 - 942 P/g product	66 - 1012 µm	Vietnam
Hussain <i>et al.</i> , (2025) [143]	103	47 (45.6%; 42.7% PE)			Pakistan
Nasrabadi <i>et al.</i> , (2025)* [153]	6	6 (mostly PE)	251 - 386 P/g mean: 298.66 ± 60 P/g	147 - 2133 µm.	Iran
Zorin <i>et al.</i> (2025) [154]	8	4			Russia

5. Realization of the Environmental Impact of Plastic MBs Stemming from Cosmetics

Several research projects incorporated questionnaires on the preferences of consumers and their usage patterns of PCCPs [60] [133] [140] [141], enabling estimates of the release of plastic microbeads from these products into wastewater systems and, subsequently, their discharge into aquatic environments via wastewater

treatment plant effluents. Thus, Chang surveyed 175 residents of a UC Berkeley student residential hall using an online questionnaire and estimated that approximately 5 kg of microplastic beads per year entered the wastewater stream from this group alone [60]. In 2011, Gouin *et al.* [155] estimated that per capita consumption of microplastics from personal care products in the United States, based on the use of polyethylene microbeads, was approximately 2.4 mg per person per day. This corresponded at the time to an estimated annual release of about 263 tonnes of polyethylene microplastics by the U.S. population. In the years 2014-2017, position papers were published by governmental institutions from Sweden [156], Norway [157], Denmark [158] and Germany [159], which approximated the release of plastic MBs due to dispersal of PCCPs into the environment (Table 9). Approximations ranged from 9 - 29 tons/year for Denmark [158] to 500 tons/year for Germany [159]. Approximations also exist for China [160] [161], the UK [25] [161], New Zealand [132] and USA [161], among others.

Table 9. Estimation of the release of plastic microparticles in form of tire wear and synthetic fibers, from personal care products and due to spillage of virgin plastic pellets in different countries.

MP source	Tire wear (Tons/year)	Synthetic fibers (Tons/year)	Personal care products (Tons/year)	Pellet loss (Tons/year)	Reference
Sweden	7670	8 - 960	66	310 - 530	(Magnusson <i>et al.</i> , 2017) [156]
Norway	4500	600	40	450	(Sundt <i>et al.</i> 2014) [157]
Denmark	4200 - 6600	200 - 100	9 - 29	3 - 56	(Lassen <i>et al.</i> 2015) [158]
Germany	60 - 11000	80 - 400	500	21,000 - 210,000	(Essel <i>et al.</i> , 2015) [159]
New Zealand	NA	NA	0.2	NA	(Gregory, 1996) [132]
China	756,240	813,000	3069	NA	(Cheung <i>et al.</i> , 2018) [160] (Kole <i>et al.</i> , 2017) [161]
UK	42,000 - 84,000	NA	16 - 86	53 billion MPs	(Kole <i>et al.</i> , 2017) [161] (Napper <i>et al.</i> , 2015) [25]
USA	1979.48	NA	263	NA	(Kole <i>et al.</i> , 2017) [161]

In the early 1970s, small polystyrene spherules, generally < 2.00 mm in diameter, were found to be widespread in coastal and surface waters of the north-western Atlantic Ocean [162] [163]. They were thought to derive mostly from spillage of virgin beads [164]. Then, there were larger, up to 5 mm or more in diameter, polyethylene and polypropylene granules. With the publications of Zitko and Hanlon [119] and Gregory [132], the public eye turned to PCCPs as one of the culprits for the PE and PP microsphere contamination of the marine environment. While nowadays the sources of MPs in the oceans are seen to be manifold,

the quantity of plastic NPs alone across the Northern Atlantic may have increased to 27 million tonnes [165]. Already, in the early 1970s, it was noted that the microspheres would most likely be ingested by many seabird and fish species, and that there would be the possibility of an intestinal blockage in these organisms [132]. The detrimental effects of MP ingestion [36] by fishes has been studied extensively [166]. Overall, the results indicate that MPs exposure significantly inhibits fish growth [167], survival, and reproductive ability, and increases oxidative damage. In addition, to the adverse effects of MPs on fishes, many of them of great commercial value, it was seen that MPs could also be transferred to humans via the ingestion of seafood [37] [38]. Equally of concern was seen the direct human exposure to MPs through skin contact, eye contact and through ingestion of MP laden toothpastes.

6. Possible Health Impacts of Plastic Microbeads and Plastic Microparticles

Reviews have appeared on potential health impacts of microplastics in general and of microplastics from cosmetics [68] [69]. It is important to distinguish between the direct effects of microplastics resulting from dermal exposure and the potential health impacts associated with their release into the environment, which may lead to human ingestion [168]. This distinction is further complicated by the ability of microplastics to adsorb and transport harmful chemical or biological substances [169]. Human ingestion is also a relevant consideration in the case of microplastic-containing toothpastes [44]. In the following, only the effects of dermal exposure to microplastics are addressed.

Dermal exposure to MPs is generally regarded as a less significant pathway of entry of MPs into the human body. Skin permeability is influenced by several factors. Particle size is particularly important: nanoplastics are more likely to penetrate the skin, whereas larger particles may enter via hair follicles, sweat glands, or through abrasions in the skin [170] [171]. It should be noted that the majority of plastic particulate matter found in cosmetic formulations is typically in the microplastic (MP) size range rather than the nanoparticle (NP) range, so that the risk of direct dermal penetration is very small.

Nevertheless, *in vitro* studies using primary skin cells have shown that nano-sized plastics can penetrate and accumulate within skin tissues, with particles up to 6 μm being taken up by keratinocytes [172]. Further research indicates that nanoplastics smaller than 200 nm can migrate through skin furrows, lipid pathways, and hair follicles, reaching the viable epidermis and, in some cases, being internalized by skin cells [173]. MPs that have penetrated the skin can potentially interact with cells and structural biomolecules.

Upon contact with the skin, these particles can elicit immune responses through the recognition of pathogen-associated and damage-associated molecular patterns by receptors expressed on keratinocytes, Langerhans cells, dendritic cells, melanocytes, macrophages, and T cells [174]. Activation of these signaling pathways leads

to the release of antimicrobial peptides and pro-inflammatory cytokines—including interleucins IL-1, IL-6, IL-10, IL-17, IL-18, and IL-22, and tumor necrosis factor (TNF)—which disrupt skin homeostasis, promote the recruitment of additional immune cells, and compromise the structural integrity of the epidermis [175] [176]. Specifically, it has been shown in an internalization experiment of PE MPs (8 μm , 1000 ng/L) in gill skin cells that PE MPs activate the NF- κB signaling pathway which centrally mediates inflammation and immune regulation and leads to an increased expression of pro-inflammatory cytokines, including TNF- α , interferon- γ (IFN- γ), IL-2, IL-6, IL-8, and IL-1 β and a concurrent suppression of anti-inflammatory cytokines such as IL-4 and IL-10 [177]. Furthermore, emerging evidence indicates that microplastics can enter cells, disrupt essential biological functions, and promote the formation of a carcinogenic microenvironment [178] [179]. These particles may contribute to carcinogenesis through multiple mechanisms, including the induction of DNA damage, oxidative stress, inflammatory responses, and disruption of cellular signaling pathways. In addition, microplastics may promote tumorigenesis through mechanisms such as endocrine disruption and genetic as well as epigenetic alterations, including changes in DNA methylation [180], histone modifications, and microRNA dysregulation [69].

7. Legislation in Regard to the Use of Solid Plastic Particles in Personal Care Products

According to Dauvergne [181], the Beat the Microbead campaign (www.beatthemicrobead.org) published that as of February 2018, nearly 450 brands across 119 companies had pledged to eliminate microbeads from their rinse-off products, which is also the number in January 2026. This promise was adopted by some of the biggest brands in the world such as L'Oréal, Colgate-Palmolive, Beiersdorf, Procter & Gamble, and Johnson & Johnson.

Table 10. Regulations of different countries or regions in respect to single use plastic in rinse off cosmetics.

Country or region	Implementation date	Regulation	Comments	References
Canada	Jan. 2018	Changes to the Canadian Environmental Protection Act	Ban on the manufacture and import of MP containing toiletries from Jan. 1, 2018 on-wards. From July 1, 2018 onwards, the ban includes all natural and non-pre-prescription drugs that contain MPs. From July 1, 2018, the sale of MP containing toiletries is banned	Government of Canada, 2023 [182] [183]
United Kingdom	Oct. 2017	At the time, newly proposed legislation	Ban prohibiting the sale and production of all those cosmetic products that have a hazardous impact on the environment	Defra (2017) [184] Hirst, D., Bennett, O. (2017) [185]

Continued

USA	July 2017/Jan. 2018	Microbeads free water act of 2015	Ban on manufacturing MP containing microbeads from July 2017 onwards and a sales ban from January 2018 onwards	H.R.1321 - 114th Congress (2015-2016) [45]
France*	Jan. 2018	Newly proposed legislation	Ban on sale and production of microplastic containing microbeads and cotton buds containing microplastics	Décret n° 2017-291 [186]
New Zealand	7-June-2018	Changes to the Waste Minimization Act of 2008	The ban states that it will be illegal to sell the microplastic containing products and a penalty will be imposed on any entity found to be involved in breaching the code of conduct	Waste Minimisation (Microbeads) Regulations 2017 [187]
Taiwan Region	July-2018 Ban on sales: (Jan. 2020)	Newly proposed legislation	The production, sale, and import of micro-plastic containing products will be banned by July, 2018	Article 21 of the Waste Disposal Act [188] [189]
South Korea	30-Nov-2023	Regulations on Safety Standards for Cosmetics	The production ban of microplastic containing products will be effective from 2017 and a ban on sales will be implemented by July 2018	Regulations on Safety Standards for Cosmetics [190]
Sweden*	1-Jul-2018	Proposed by the Swedish Chemical Agency	Ban on production, import and sale of microbeads in cosmetic products	Förordning (1998:944, 4-4b §§) om förbud m.m. i vissa fall i samband med hantering, införsel och utförsel av kemiska produkter [191]
India	1-Jan-2020	Proposed by Bureau of Indian Standards	These rules, under the Drugs and Cosmetics Act, govern the manufacture, import, and sale of cosmetics in India. However, they do not explicitly ban MPs like plastic MBs in PCCPs	Amendment No. 2 November 2017 to IS 4707 (Part 2): 2017 Classification of cosmetic raw materials and adjuncts Part 2 List of raw materials generally not recognized as safe for use in cosmetics: Item 1373. [192] [193]
Pakistan		Ministry of Climate Change & Environmental Coordination	Although there is a regulation on single use plastics, there is no specific regulation on MP containing cosmetics	S. R. O. 935(I)/2023. Single Use Plastics (Prohibition) Regulations [194]

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Italy*	1-Jan-2020	Article 180, paragraph 1i of Legislative Decree No 152 of 2006	A ban on the manufacturing of cosmetic products containing MPs	
Ireland*	20-Feb-2020	Microbeads Prohibition Act 2019	The act prohibits the manufacture and sale of cosmetic products in Ireland markets	EPA, 2025 [195]
Thailand	1-Jan-2020	Proposed by Ministry of Public Health in Thailand	A ban on sale, production and commercialization of new cosmetic products in Thai markets has been announced	
Netherlands*	1-Jan-2014	Agreement with the cosmetics industry	Voluntary phaseout of plastic microbeads in rinse-off cosmetics	
Portugal*	30-July-2021	Decree-Law 69/2021 (Official Gazette)	Prohibition of the distribution, consumption and use of certain cosmetics that have intentionally added microplastics $\geq 0.01\%$	
Argentina	29-12-2022	Law 27602	Ban on production, import and commercialization of cosmetic products and containing intentionally added microplastics	
Australia	2022 (delivery date) Started July 1, 2018	Action 5.6 of the National Waste Policy Action Plan, Australia	Voluntary phaseout of microbeads in rinseable PCCPs. The states NSW (2022), ACT (2024), Queensland (2022), and Western Australia (2023) have legislated bans as part of bans on single-use plastic	qld.gov.au (2025) [196] ACT (2024) as part of the Circular Economy Act 2023 [197] NSWepa (2025) [198]
Chinese Mainland	31-Dec-2020/31-Dec-2022	Proposed by China National development and reform commission (NDRC) Notice [2020] No.80	The ban prohibited the production of microplastic containing products from 31 December 2020 and sale will be prohibited by 31 December 2022	Xinhuanet (2020) [199]
EC	Sept., 2023	Commission Regulation (EU) 2023/2055	Restriction on the use of MPs in PCCPs with a focus on microbeads and glitter particles. Present stocks may still be sold. PCCPs containing MPs (glitter, and for other uses) may be sold until mid Oct. 2027 (for rinse-off cosmetics), until mid Oct. 2029 (for leaveon cosmetics) and until mid Oct. 2035 for nail polish, lip and makeup products	European Commission 2025 [200]

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South Africa	Aug., 2025	Ministry of Forestry, Fisheries and the Environment	Draft regulations to the production, distribution, sale, import, and export of plastic microbeads and products containing them. There is to be a 24 transitional period after the announcement of the ban	Media release of the Ministry of Forestry, Fisheries and the Environments, Republic of South Africa [201]
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* As an EC member state, the country follows the Commission Regulation (EU) 2023/2055.

As early as in 2014, the Netherlands, Austria, Belgium and Sweden issued a joint call to ban the use of microplastics in cosmetics to protect marine life. At the same time, the Dutch government implemented a voluntary industry agreement with cosmetic manufacturers and retailers. for the phase-out of microbeads in rinse-off products sold in the Netherlands. It was highly successful—by 2016, over 90% of such products were microbead-free. Also, in 2014, Illinois became the first jurisdiction in the world to ban products from containing microbeads. This set a precedence for eight other US states [Colorado, Wisconsin, Indiana, Maine, Maryland, New Jersey, Connecticut and California] and the American federal government to enact similar laws. The state of California became the first jurisdiction in the world to ban the use of all microbeads, including biodegradable microbeads. In 2015, the province of Ontario formulated Bill 75, Microbead Elimination and Monitoring Act, 2015 [202], which would prohibit the manufacture of microbeads and the addition of microbeads to cosmetics, soaps or similar products. In addition, the bill would require the province to conduct water sampling for microbeads in the Great Lakes. Canada as a whole followed suit in 2018, imposing a ban on MP containing toiletries. As in many other countries and regions, the ban was preceded by a comprehensive introduction to the planned regulation and consultation documentation with a 75-day public comment period [203], including a document on the status of scientific knowledge in respect to the interaction of plastic microbeads and the environment [204]. EC-restrictions in regard to microplastics are currently governed by Commission Regulation (EU) 2023/2055 [200] and amends Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). In South Korea, microplastics used as raw materials in cosmetics such as bathing and cleaning products were forbidden according to the “Regulations on Safety Standards for Cosmetics” as of July 2017 [205] [206]. According to Lee and Kim [205], cosmetic products manufactured prior to this regulation continued to be sold for some time, at least in 2018. Therefore, it was seen that despite the prohibition, microplastics continued to discharge into sewage treatment facilities (STFs) from personal care products. In June 2023, South Korea proposed the Special Act on Microplastic Reduce and Control, which aims to comprehensively manage microplastic usage and emissions, which prohibits the manufacture and import of products containing micro-

plastics above safety thresholds. Meanwhile, Australia - Australia has implemented a voluntary industry phase-out but not a ban of plastic microbeads in rinse-off cosmetics and personal care products since 2018. This includes products like exfoliants, cleansers, and toothpaste [207]. **Table 10** shows a list of regulations forwarded by different governments.

Many government bans limit themselves to rinse-off cosmetics, but do not touch microplastics when they are liquid polymers and powdered plastics used in makeup foundations, sunscreens, hair gel, and eye drops [208]. Also, most of the research on plastic particle content in cosmetics has focused on rinse-off products (**Table 8**), including toothpastes [138] [142]. It is here that Kukkola *et al.* [209] have warned that MP containing leave-on products are widely understudied, that a uniform methodology of MP identification from leave-on products is, for the most part lacking and that regulations and monitoring of these products are largely missing. The first explicit inclusion of leave-on PCCPs in microplastic-related guidelines occurred in the Nordic Swan ecolabel criteria [210], established in 2010. The Nordic Swan is a voluntary ecolabel awarded to products and services that meet high environmental standards across their life cycle, with the objective of promoting sustainable development and environmentally conscious consumer choices. This initiative was followed by the introduction of similar provisions in the EU Ecolabel in 2021 (EU 2021/1870) [211]. The incorporation of microplastics in leave-on PCCPs within ecolabel schemes reflects a growing awareness of their presence in such products and their potential environmental impacts. This progression culminated in the first binding legal framework addressing microplastics in leave-on PCCPs, introduced through the September 2023 amendment to the REACH Regulation (EC No 1907/2006) [212]. This amendment added synthetic polymer microparticles to the REACH Restrictions List (Annex XVII), thereby prohibiting the intentional addition of microplastics to products placed on the EU market. The amendment states a transitional period of 12 years for the ban on placing on the market of MP containing leave-on products. This affects especially make-up, lip and nail products.

Overall, legislation addressing plastic microparticles in PCCPs, including rinse-off cosmetics, remains highly heterogeneous. This variability is particularly evident in the implementation and enforcement of existing regulations. International trade between regions with established bans on microplastics and those without such restrictions further complicates regulatory effectiveness. This challenge is illustrated by the study of Not *et al.* [213], which examined products purchased in regions where bans had already been implemented (e.g., Canada and the UK), where bans had been announced but not yet enforced (e.g., Italy), and where no restrictions had been introduced (e.g., Hong Kong SAR and Japan). Notably, PE MPs were detected in products obtained from all three regions.

The state of New South Wales, Australia, was one of the first jurisdictions to penalize wholesalers, manufacturers and distributors, when issuing non-compliance notices to six businesses in regard nine different MP carrying cosmetics on the shelves. Failing to comply with a Compliance Notice carries a maximum pen-

alty of up to A\$550,000, plus A\$55,000 for each additional day the offence continues [214].

8. Development of Substitutes for Cleansing Plastic Microbeads, Synthetic Polymeric Thickeners, Stabilizers, and UV Filters

Development of cosmetic formulations has always been ambivalent, one route utilizing synthetic polymers, the other making do without for many of the needed components. This includes the time period between the early 1990s and the 2010s. It must be noted that microcrystalline wax appearing on the EU Cosmetics Ingredient Database (CosIng) under the INCI name Microcrystalline Wax/Cera Microcristallina is still commonly used as a binding, viscosity-controlling, and emollient ingredient in creams, lipsticks, balms, and other cosmetics as there is no general ban on its use in cosmetics under Regulation (EC) No. 1223/2009. Its use in cosmetics is also allowed in USA. As the wax derives itself from petroleum refining, being composed mainly of branched and cyclic saturated hydrocarbons, albeit of smaller molecular mass than PE and of lower melting point (60 - 90°C vs. 100 - 110°C for PE), regulatory bodies generally require that cosmetic-grade microcrystalline wax is highly refined to reduce impurities such as polycyclic aromatic hydrocarbons (PAHs).

A look into **Table 11** shows typical patent applications utilizing microbeads based on inorganic material and polysaccharide material both as cleansing particles and as rheological modifiers. These efforts continue in the 2020s (**Table 12**). Polysaccharides used include cellulose, starch, alginate, chitosan, pectin, agar, xanthan gum, guar gum, and hyaluronic acid. Many of these materials are also utilized in microparticulate or powdered forms, owing to their film-forming and emulsifying capabilities, as well as their capacity to modify formulation rheology [215]. In addition, several polysaccharides exhibit beneficial functional properties, such as antimicrobial activity (chitosan; [216]), antistatic effects (cellulose; [217]), moisturizing capacity (chitosan; [216]), and skin-protective effects (hyaluronic acid; [218]). Some of the polysaccharides used are synthetically modified such as carboxymethylcellulose (CMC), which can be prepared as its sodium salt via the etherification of cellulose with sodium monochloroacetate in an alkaline solution (NaOH). CMC is a versatile ingredient in both cleansing agents and cosmetics. It serves as a thickening agent, stabilizer, emulsifier, and film-forming agent. CMC microbeads are used improve the texture and feel of cosmetic formulations.

As an example of the production of environmentally benign alginate microbeads to be used as scrubbing additives, Ca-alginate MBs of 540 to 1120 µm size were fabricated by electro spraying an aqueous alginate solution into distilled water containing calcium ions [219]. Ca- and Ba-alginate microspheres as delivery systems for active ingredients in cosmetics were investigated in the presence/absence of surfactant in oil-in-water (o/w) emulsions [220]. Kozłowski *et al.* [221] developed

spherical microparticles made of sodium alginate and a mixture of sodium alginate and starch using encapsulator BÜCHI B-395.

Chitosan's capacity to interact electrostatically with negatively charged substrates, such as skin or damaged hair, leading to the formation of polymeric films that enhance conditioning and moisturization, makes it an excellent candidate for skin and hair care formulations [222]. Chitosan microbeads have also been proposed for use as drug delivery system [223]. Ju *et al.* [224] prepared microbeads from chitosan via an inverse emulsion system using sorbitan monooleate (Span® 80) as a non-ionic surfactant. Thereafter, the amino functions on the surface of the prepared microbeads were acetylated with acetic acid anhydride. These so-called cito-beads with a narrow size distribution of 280 µm possessed a better skin-cleansing efficiency than commercially available plastic MBs.

Table 11. Patents in regard to the development and manufacture of microbeads/microparticles with useful applications in cosmetics that do not contain plastic materials.

Inventor	Assignee	Country of application	Application date	Granted date	Patent number	Description
D. Cremer [225]	Individual	Germany	Dec.24 th , 1973	July 3 rd , 1975 (published)	DE 2364643A1	Vaporization and drop formation technique for the preparation of microspheres such as of glass microspheres, also for use in cosmetics
M. Horino and T. Uramoto [226]	Pola Orbis Holdings Inc	Japan	June 16 th , 1978	Dec. 26 th , 1979 (published)	JPS 54163830A	Cosmetics containing metal silicates, carbonates, tungstates, oxides, or hydroxides as spherical granules
S. Wiecehers <i>et al.</i> [227]	Evonik Industries AG	USA	Feb. 4 th , 2013	April 23 rd , 2015 (published)	US 2015O11084 1A1	Use of powdered cellulose in cosmetic applications
Y. Funabiki and D. Nishiyama [228]	Sumitomo Seika Chemicals Co Ltd	Japan	March 23 rd , 2017	June 2 nd , 2021	JP 6879999B2	Preparation of cellulose granules to be used in cosmetic applications

Table 12. Recent patents showing the breadth of the use of naturally sourced material, including oligosaccharide, in cosmetics as thickeners, stabilizers, anti-aging/anti-wrinkling agents and as part of UV filters.

Inventor	Assignee	Country of application	Application date	Granted date	Patent number	Description
I. Bonnet <i>et al.</i> [229]	BASF Beauty Care Solutions France SAS	France	Nov 25 th , 2012	July 3 rd , 2015	FR 2997406B1	Hyaluronate and glucomannan polymer microbeads as antiwrinkling agent in a topically applied cosmetic

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X. Qiu <i>et al.</i> [230]	South China University of Technology SCUT	USA	Nov. 21 st , 2017	Aug. 4 th , 2020	US10729624B2	Highultraviolet absorption lignin/chemical sun-screening agent microcapsule
T. Tsuji and T. Nogita [231]	Chuetsu Pulp and Paper Co Ltd	USA	April 18 th , 2018	Sept. 23 th , 2025	US 12419825B2	Surface-hydrophobicized cellulose nanofibers for oily thickener to be used in cosmetics
G. Diste-fano and P. Valsesia [232]	Intercos SpA	USA	March 1 st , 2021	March 23 rd , 2023 (published)	US 20230086493A1	Chemically modified cellulose particles (5 - 60 microns) used in cosmetic formulations
D. Schlenker <i>et al.</i> [233]	Beiersdorf AG	USA	Jan. 14 th , 2021	March 16 th , 2023	US 20230083509A1	Polyacrylate-free cosmetic preparation
M. Haraguchi Padilha <i>et al.</i> [234]	Botica Comercial Farmaceutica Ltda	USA	Dec. 22 nd , 2021	May 5 th , 2024	US 20240173224A1	Lignin composition associated with ZnO and TiO ₂ used in cosmetics to protect skin against oxidation and UV radiation
S. Scheele <i>et al.</i> [235]	Henkel AG and Co KGaA	USA	July 10 th , 2020	July 18 th , 2023	US 11701321B2	Solid hair cosmetic composition with naturally sourced cellulose

O'Brien *et al.* [236] developed spherical cellulose microbeads using a scalable membrane emulsification phase inversion process as an environmentally friendly alternative to plastic microbeads. Patents have forwarded the use of commercially available cellulose granules (such as KC Flock W-400TM or W-100TM, manufactured by Nippon Paper Ind.) as abrasive agents in cleansing products [228] [237] [238]. More recently, bacterial cellulose (BC) has gained attention in this field due to its high purity, porosity, and tensile strength. BC has the same chemical composition as plant-derived cellulose, differing only in molecular weight [239]. This polymer has been explored for use in cosmetic applications, including personal care formulations, and facial scrubs [240].

Thus far and in general, compared with synthetic polymer beads, natural alternatives used in cosmetics often provide milder and less uniform abrasiveness due to their irregular shape and variable hardness, which can reduce exfoliation consistency. However, these natural materials are frequently perceived as offering a more pleasant, skin-friendly sensory feel, albeit with greater batch-to-batch variability than synthetic beads. The inclusion of newly developed microbeads/microparticles in cosmetic products will depend on the ease of sourcing and on cost. Further development of regulatory frameworks will shape the future evolution of cosmetic ingredients and remains essential for ensuring consumer health and safety.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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