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Cellulose acetate technology to replace banned PE beads

KEYWORDS: PE beads alternative, exfoliant, cellulose acetate.

Abstract

To replace polyethylene (PE) beads with renewable and biodegradable scrubs, cosmetic formulators have to consider several characteristics of the different materials available on the market that appear to be similar to PE in terms of colour, abrasiveness, suspension capacities, cost effectiveness, stability in various products, worldwide regulatory approval, etc. The traditional exfoliating ingredients from plants and minerals have not given totally satisfactory results for replacing PE because their characteristics were not similar. The latest product created and based on cellulose acetate fills the gaps left by the other products.
This review explains the origin of the first bio-based polymer, cellulose acetate, created during the 19th century. This polymer is made from pure cellulose extracted from wood pulp by a reaction using acetic acid. Cellulose acetate is biodegradable and is a highly sustainable product with no impact on agricultural land. The use of cellulose acetate as an exfoliant was studied with the product known asCelluloscrub^{TM}. This study concerns its capacity to replace PE and also its stability in the cosmetic products used for making scrubs.

INTRODUCTION

Microplastics are used extensively in personal care products for exfoliation purposes. The microbeads used in personal care products are mainly made of polyethylene (PE), but can also be made of polypropylene (PP), polyethylene terephthalate (PET), polymethyl methacrylate (PMMA) or nylon. In recent years, the potentially negative impact of microplastics on the environment has been explored and this has led to the decision by some cosmetic companies to remove microplastics from their formulations.

Cosmetics formulators have to take several characteristics into consideration when replacing synthetic polyethylene (PE) beads with natural and biodegradable scrubs;

- Particles should have the same visual effect (white colour)
- Skin feel and abrasion capacities should be similar
- Particles should have the same suspension capacity
- Stability should be equal to that of PE. The colour stability of particles must be perfect and the abrasiveness unchanged even in surfactant gel. In addition, the formulation should not be impacted (pH, viscosity, etc)
- Global consumption of PE beads in cosmetics amounts to several hundred tons. So the products used to replace PE beads must be available in large quantities and at an affordable price
- Global marketing of the product, with universal approval, is another key point

The traditional exfoliating ingredients presents both advantages and disadvantages to be used instead of PE.

At first particles from plant or mineral origins were used for centuries prior to PE becoming. Stone fruits *(apricot, almond, walnut, cherry, olive, etc)* are widely used as scrubs for cosmetic use as they give a very natural image to cosmetic products and they are usually cost-effective. But due to their dark colour, stone fruits could not easily replace PE beads without considerably changing the colour of the cosmetic product.

Particles of mineral origin *(pumice, sand and other minerals)* can be white in colour. These scrubs are too abrasive, as well as having a high density (volumetric mass) which requires a change of formula to keep them in suspension.

One of the first technologies that was developed a few years ago from biopolymers was polylactic acid. This is a biopolymer manufactured from corn starch that has the advantage of being

Figure 1. Microscopic picture of stones fruits.

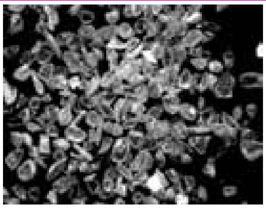

Figure 2. Microscopic picture of minerals particles.

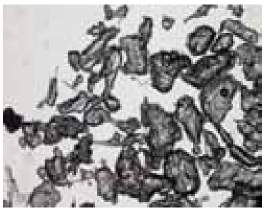

Figure 3. Microscopic picture of polylactic acid particles.

biodegradable and having a perfect white colour similar to polyethylene. But the colour stability is not guaranteed as products become yellowish. In addition, lactic acid is released so that the pH value of the cosmetic products decreases dramatically.

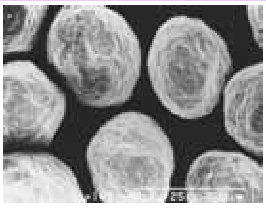

Figure 4. Microscopic picture of microcrystalline cellulose particles.

Following this, scrubs manufactured from microcrystalline cellulose were developed. This scrub has good sustainable properties but cannot be used successfully to replace PE due to its poor stability in water and lack of abrasiveness. Exfoliating powders manufactured with silica combine white colour particles and cost-saving benefits. However, silica lacks strength and is easily crushed by the fingers during use. Wax beads are a good technological alternative and are available in a variety of sizes, colours and hardness. The foremost disadvantage of using wax-based technology is the high cost.

Figure 5. Microscopic picture of cellulose acetate particles.

The new Celluloscrub cellulose acetate technology presented below is the only technology that presents all the characteristics required from an alternative to PE beads.

CELLULOSE ACETATE – A BIO-BASED MATERIAL WITH A CENTURY OF HISTORY

We are in the age of plastics. Although today these plastics are polymers obtained mainly from fossil carbon molecules extracted from petrol oil, they were made at first from organic bodies extracted from renewable resources.

Figure 6. Manufacture of Cellulose acetate (by La Nature, 1903).

In 1865, Paul Schutzenberger presented a report to the Academy of Science on the action of acetic acid on cellulose. This marked the discovery of cellulose acetate. Cellulose acetate aroused certain industrial interest as early as the 1890s. From 1903 it was used in industry to manufacture plastics and rayon, an alternative textile to silk. It was thus the first plastic material used industrially. A new industry was born thanks to cellulose acetate making objects such as combs and knitting needles. After the Second World War, plastics derived from oil gradually replaced cellulose by-products for reasons of cost. Unfortunately, the environmental characteristics of oil by-products are less attractive than those of cellulose derivatives because their raw material is neither renewable nor biodegradable. The use of cellulose acetate in cosmetics is thus the industrial application of a material known for more than a century and whose characteristics correspond to 21st century requirements concerning renewability and biodegradability (1, 2).

Cellulose acetate is derived from cellulose by deconstructing wood pulp into purified white cellulose. The cellulose is then reacted with acetic acid and acetic anhydride in the presence of sulfuric acid. It is then put through a controlled, partial hydrolysis to remove the sulfate and a sufficient number of acetate groups to give the product the desired properties (3).

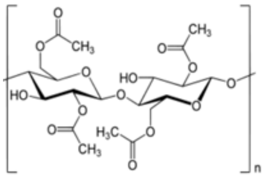

Figure 7. The chemical structure of Cellulose acetate.

The basic material for cellulose acetate, plant cellulose, is the most readily available renewable material on the planet. The wood pulp raw material is sourced exclusively from renewable and carefully managed forestry plantations, where there is systematic replanting after harvesting. The manufacturing process itself is designed to minimise the use of chemical and water at every stage, recovering and reusing them wherever possible and keeping quantities of chemicals to the lowest possible levels. And at the end of its life the finished product, cellulose acetate, is biodegradable (3).

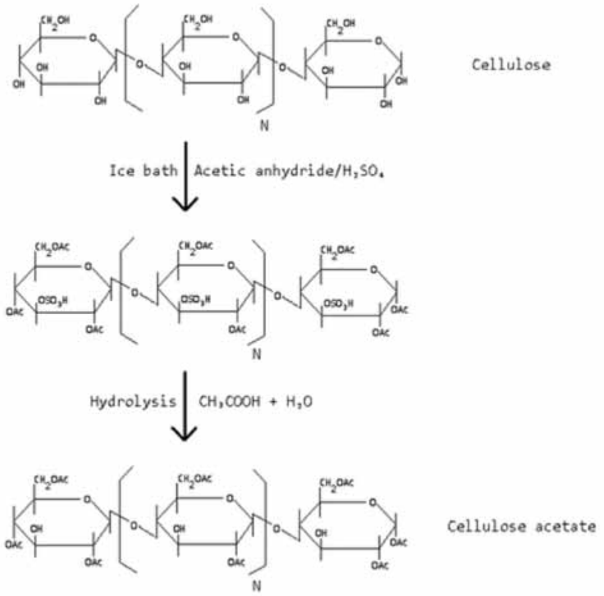

Figure 8. Cellulose acetate preparation.

Celluloscrub™ Celluose acetate has no impact on agricultural land used for growing food as the main purpose of agriculture is to nourish the human population. Other natural ingredients are directly derived from food (rice, etc) or from processed food. For instance, some materials are manufactured by biosynthesis from corn starch (e.g. polylactic acid) which may have an impact on the availability of food for the human population.

BIODEGRADABILITY OF CELLULOSE ACETATE

Within the scientific community cellulose acetate is generally recognized as a biodegradable polymer. Microbial degradation has been extensively studied and it has been found that to achieve polymer decomposition, biodegradation requires two steps. The first step is to remove the acetyl group which is accomplished by microbial enzymes. Acetyls are common functional groups on natural products and thus enzymes to remove them are readily available in microbes. The cellulose is subsequently broken down further by other microbial enzymes that are widely used in natural environments to degrade plants. Many studies have shown that biodegradation of cellulose acetate occurs in a variety of environments including soils, composts and wastewater treatment facilities (4).

A study was conducted to measure the biodegradation of cellulose acetate films : a cultivation technique using in vitro enrichment and an activated sludge wastewater treatment system. The enrichment culture was able to degrade Cellulose acetate films within 2–3 weeks, as indicated by a 67% weight loss. The industrial wastewater treatment system provided the same level of degradation within 10 weeks (5).

In 1993, Gu, Eberiel, studied the biodegradability of Cellulose acetate films under controlled composting conditions. The materials were exposed to biologically active laboratory aerobic test vessels. They found that the films completely disappeared after incubation periods of 7 and 18 days respectively. The authors of this study stressed that both aerobic and anaerobic microorganisms are known to produce the complete set of hydrolases, including esterases, which are necessary to degrade naturally occurring acetylated polysaccharides (6).

Cellulose acetate fibres also proved to be anaerobically degradable when measured according to ASTM D 5210-91 and ISO 11734 [7]. The determination of anaerobic degradability is based on the liberation of biogas using diluted digested sludge as the inoculums. The study demonstrated that after 3 weeks in the ASTM medium, 60–70% of the initial Cellulose acetate as well as of the cotton reference material was degraded (7).

SENSORY TEST OF CELLULOSCRUB™ CELLULOSE ACETATE TECHNOLOGY

Polyethylene has historically been a source of highly effective exfoliation that is non-irritating to the skin. The data below demonstrates that Celluloscrub™ cellulose acetate is a viable green alternative to the widely used polyethylene scrubs.

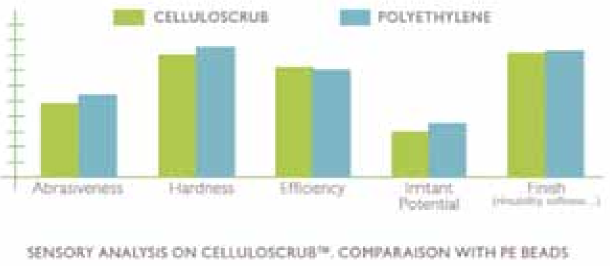

Figure 9. Sensory analysis on Celluloscrub – Comparison with PE beads.

	Time	Abrasiveness	Odour	Product colour	Scrubs particles colour	Volumic mass	Viscosity (mPa.s) Brf-20 trs/min	Total aerobic plate count	pH
Samples	J0		none	Transparent with white particles	white	1050 g/l	44 000	<10 CFU/g	5,4
Sample A	1 month	unchanged	none	unchanged	unchanged	1050 g/l	36 000	<10 CFU/g	5,1
	6 months	unchanged	None	unchanged	unchanged	1050 g/l	37 000	<10 CFU/g	5,2
	12 months	unchanged	None	unchanged	unchanged	1050 g/l	35 000	<10 CFU/g	5,1
Sample B	1 month	unchanged	None	unchanged	unchanged	1050 g/l	38 000	<10 CFU/g	5,1
	6 months	unchanged	None	unchanged	unchanged	1050 g/l	39 000	<10 CFU/g	5,1
	12 months	unchanged	None	unchanged	unchanged	1050 g/l	36 000	<10 CFU/g	5,0
Sample C	1 month	unchanged	None	unchanged	unchanged	1050 g/l	37 000	<10 CFU/g	5,1
	6 months	unchanged	None	unchanged	unchanged	1050 g/l	35 000	<10 CFU/g	5,1
	12 months	unchanged	none	unchanged	unchanged	1050 g/l	38 000	<10 CFU/g	5,2

Figure 10. Stability results in a shower gel.

2 exfoliating creams have been prepared : One with 5% of Celluloscrub 300 microns ; An other one with 5% of PE beads 300 microns.
12 participants were asked to apply the creams on the face and to evaluate differents criterions : abrasiveness, hardness, efficiency, irritant potential and the finish on the skin. The participants have to evaluate the differents criterions on a scale of 1 to 10, with 10 being excellent and 1 being poor.

The panel study indicated that the Celluloscrub^{tm} cellulose acetate and polyethylene exfoliants had similar effects.

STABILITY TEST CELLULOSCRUB^{TM} CELLULOSE ACETATE TECHNOLOGY

Stability studies with Celluloscrub^{tm} have been carried out to verify whether it interferes with the stability of cosmetic products. The cosmetic formulations that have been tested are an aqueous gel, a shower gel, an emulsion and an oily gel. Each of these products contain from 5 to 10% of Celluloscrub 500.

Three samples from each formulations are prepared and placed in three different conditions

- Sample A is placed in an aging oven at 55°C
- Sample B is place at ambient temperature (20°C) and away from light
- Sample C is placed at ambient temperature (20°C)and under the sunlight

The evaluation criteria are abrasiveness, odour, colour, density, viscosity, microbiology and pH. The different criteria were measured three times over a period of
one year. The abrasiveness, odour, colour were evaluated by panel members. The density was analysed by a viscometer, the pH by a pH-meter.

The figure 10 indicates the stability study of the shower gel formulated with 8% of Celluloscrub.
In the sability study, no modification of organoleptic properties was observed and they comply with specifications during the study. The small variations in pH are not significant and conform to product specifications. The microbiology results comply with specifications regardless of storage conditions. The abrasiveness of the product is unchanged. We can conclude that the abrasiveness of Celluloscrub^{tm} remains unchanged. Based on the results obtained and what is generally known about this kind of cream, we conclude that the stability of this cream is not impacted by Celluloscrub^{tm}.

Stability studies made with Celluloscrub^{tm} show an optimal stability in all cosmetic products. One of the most important advantages of Celluloscrub^{tm} is its very low impact on the pH value of cosmetic products. With Celluloscrub^{tm}, the pH value is not reduced by more than 0.1 to 0.2. With other natural polymers, such as polylactic acid (PLA), the pH value is more impacted (around 1.0).

CONCLUSION

It appears that cellulose acetate biopolymer is the best raw material to manufacture exfoliating ingredients designed to be used in cosmetic formulations. Cellulose acetate has similar characteristics compared with polyethylene. Furthermore, the big difference compared with PE beads is that cellulose acetate is biodegradable and comes from a renewable origin. Compared with all other raw materials used to manufacture exfoliating ingredients, cellulose acetate is the only one that presents all the same characteristics as PE including regulation, raw material availability and cost.

Bio-plastics from petroleum have been developed since the mid-20th century. Their impact on the environment has been extremely negative. As they are not biodegradable, future generations will find plastic inside geological deposits. The "discovery" of the industrial use in cosmetics of this polymer which has existed for more than 100 years demonstrates that there are green solutions around us which can be used to avoid the destruction of our environment.

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