

VTT Technical Research Centre of Finland

## Review on polymers applied in paper making in respect of plastic definition

Harlin, Ali

Published: 16/06/2020

*Document Version*  
Publisher's final version

[Link to publication](#)

*Please cite the original version:*

Harlin, A. (2020). *Review on polymers applied in paper making in respect of plastic definition*. VTT Technical Research Centre of Finland.



VTT  
<http://www.vtt.fi>  
P.O. box 1000FI-02044 VTT  
Finland

By using VTT's Research Information Portal you are bound by the following Terms & Conditions.

I have read and I understand the following statement:

This document is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of this document is not permitted, except duplication for research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered for sale.

# Review on polymers applied in paper making in respect of plastic definition

Research Professor Ali Harlin  
VTT Technical Research Centre of Finland  
16 June 2020

**beyond the obvious**



# Review on polymers applied in paper making in respect of plastic definition

Research Professor Ali Harlin, VTT Technical Research Centre of Finland

**To be or not to be, that is the question – not just about classification but also directing the future development of materials, applications and design. It is also essential for legislative actions and to follow the implementation of the acts.**

The motivation for this short literature review is to understand the impact of a novel definition of plastic for papermaking developed for the Single Use Plastic directive as follows: *“plastic” means a material consisting of a **polymer as defined in section 5, Article 3 of Regulation (EC) No. 1907/2006**, to which additives or other substances may have been added, and which **can function as a main structural component** of final products, with the **exception of natural polymers that have not been chemically modified.**’*

Furthermore, there is the concern of how the definitions of different materials will be applied in future EU legislation, especially those related to the EU Circular Economy Action Plan.

It is obvious that paper and board have several benefits as materials, and they are essential for a sustainable economy. It is vitally important that the definitions of plastic and paper are clear and they should not be mixed with each other.

## Summary of basic findings

Plastic is found 4.6 times more in beach litter compared to its share of overall use, due its slow degradation and accumulation. One main reason for this is that the recycling of paper and board is well established, feasible and technically viable. Second, paper and board products are not found floating in the sea due to their ability to disintegrate in water. Third, paper and cardboard are responsible for less than 2% of all microplastics.

When defining plastics, everything but naturally-occurring polymers is confusing due to several issues raised by the definition of semi-synthetics and composites. Firstly, it may sound logical to say that the chemical modification of natural polymers makes them semi-synthetic materials. However, chemical reactions such as hydrolysis and oxidations also occur in nature. In addition, modified polymers in many cases still act as natural ones and are not denaturalised. This leads to the conclusion that we should also allow semi-synthetic polymers based on case-by-case studies and approve their use for purposed applications.

Secondly, paper and board materials are all composite materials mainly made of natural fibres that are able to disintegrate in water and can be recycled by means of repulping, and certain papermaking chemicals that are used as essential additives for manufacturing, converting and applications. This means we should nominate an upper level of polymer additives for papermaking and converting.

## Proposed definitions

**Paper** is a repulpable (meaning that it disintegrates in water) web that optionally contains inorganic fillers, less than 10 per cent of its weight of organic additives (including polymers or plastics), and essentially is made of natural fibres forming hydroentanglements enabling the reuse of the fibres in similar products.

## Background

**Plastic** is a composition essentially made of high polymers with a number of optional fillers and additives with an average molecular weight  $M_n < 1500$  at least 10 weight percent, possible to be converted by heat and pressure.

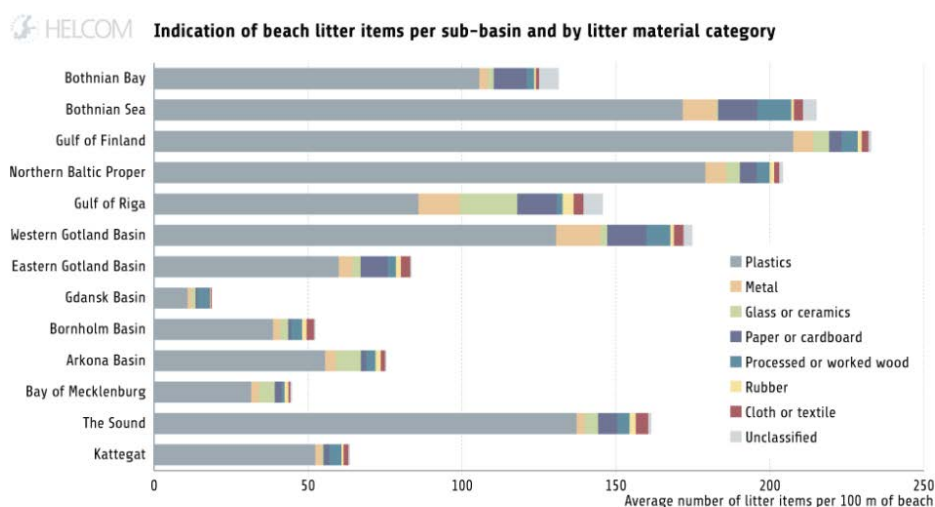
Background

**Plastics** and polystyrene foam (Styrofoam) comprise 90% of all **marine** debris, with single-use food and beverage containers being one of the most common **items** found in **ocean** and coastal surveys. The issue of disposable cups in the sea relates particularly to polystyrene PS foam cups and lids. The proportion of litter materials collected on different types of beaches is 67% and 7% for different plastics and paper and cardboard respectively. The amount of paper and board relates to roughly half of all degradable litter.

Material (%)	Type of beach		
	Urban	Rural	Peri-urban
Plastic	59	50	53
Foamed plastic	8	4	5
Organic	2	2	3
Glass & ceramic	6	14	10
Wood	4	5	4
Rubber	1	3	1
Metal	8	5	10
Paper & cardboard	7	5	10
Cloth	3	3	2
Other litter	2	9	2

Table 1 - Proportion (in %) of litter materials collected on the different types of beaches sampled within the MARLIN project. (Source: elaborated from MARLIN, 2013).

The monitoring of beach litter at the Baltic Sea regional scale reveals that the observed proportion of paper and cardboard litter is markedly low – in fact it is barely measurable. Of all the packaging brought to the market in 2017, 35% was paper and cardboard, while plastic accounted for 18%. Simultaneously, recycling rates were up to 80% and 18% respectively. According to calculations, it could be expected that 14.5% of plastic and 7% of cardboard would end up as litter. However, the amount of plastic in the region is 4.6 times higher, due to its slow degradation and accumulation.



We do not have reliable documentation on paper and cardboard on the sea bed and in sediments. The obvious reason for this might be that the pulp-based materials are water repulpable and disintegrate in water conditions. This is due to the hydroentanglement of fibre in a web structure. A second observation is that materials disintegrating in water have a limited ability to form floats in the sea and travel long distances.

## Paper-originated microplastic

It has been shown that plastic-coated paper does not degrade in compost<sup>i</sup>. The Danish Ministry of Environment and Food has studied the occurrence of microplastics. According to the study, paper is not recognised as a source of released microplastic. The main secondary sources mentioned are tyres, textiles, paints, road markings and building materials, which represent 55.8, 6.2, 7.7, 4.1 and 2.9% of all sources of microplastics respectively<sup>ii</sup>. This means paper and cardboard is responsible for less than 2% of microplastics.

	Total emission t/year	% of total (average) **	Emission to sewage treat- ment plants (STP) t/year	Ultimate emission to the aquatic environment * t/year	% of total ultimate emission to the aquatic environment (average)**
<b>Secondary microplastics</b>					
Tires	4,200-6,600	55.8	1,600-2,500	500-1,700	60.2
Textiles	200-1,000	6.2	200-1,000	6-60	1.8
Paints (excl. ship paints)	150-810	5.0	14-220	6-149	4.3
Ship paints	40-480	2.7	0-50	21-240	7.1
Road markings	110-690	4.1	40-260	10-180	5.2
Building materials of plastics	80-480	2.9	30-150	4.5-37.5	1.2
Footwear	100-1,000	5.7	40-380	10-260	7.4
Cooking utensils, scouring sponges and cloths	20-180	1.0	20-180	1-50	1.4
Other uses	100-1,000	5.7	20-500	8-375	10.5
<b>Total, secondary microplastics (rounded)</b>	<b>5,000- 12,200</b>	<b>89.0</b>	<b>2,000-5,200</b>	<b>600-3,100</b>	<b>99.1</b>
<b>Total quantified microplastics (rounded)</b>	<b>5,500-13,900</b>	<b>100</b>	<b>2,000-5,600</b>	<b>600-3,100</b>	<b>100</b>

## Comparing plastics to non-plastic materials

In many contexts, plastics are understood to be synthetic polymer materials that are mouldable, typically at elevated temperatures. However, the definition is not exact, because plastics form a wide range of [synthetic](#) or semi-synthetic [organic compounds](#) that are [malleable](#) and so can be [moulded](#) into solid objects. Rubbers are also occasionally included in the same group as plastics.

According to the IUPAC definition, plastics are expressed in ISO 472:2003 as *mixtures comprising essentially of high molar weight polymer, which are shaped by flow at some stage of their manufacturing.*

High molar weight is defined typically in polymer science according to the physical state of the polymeric material, which means higher molar mass than is typical in respective wax, e.g. in polyethylene wax, the number of monomer units  $n=500-1000$ .

The word *essentially* has not been clearly defined, but it can be understood to mean that the material mainly contains the high molar weight polymer. One consideration is that the properties of the mixtures change essentially. However, the mixtures should be made of real blends of polymers and additives, not composite materials.

	Non-plastic	Grey area polymers	Plastic
<b>Reference</b>	<i>Ref. Environ. Sci. Technol 2019, 53, 1039-1047, fig2, // Chem.Soc.Rev., 2017, 46(22), 6855-6871: essential natural polymer</i>	<i>IUPAC recommendation 2008; RSC Publ. Cambridge, 2009; p. 443: relatively high molar mass of repetition of molecular units</i>	<i>ISO 472:2013, Plastics Vocabulary: essentially high molar weight polymer shaped by flow</i>
<b>Chemical composition</b>	Naturally occurring (wool, silk, cellulose) Natural polymers REACH Article 3(40) Dissolving pulp Hydrolysed starch	Rubber Plasticised (PVC) Inorganic/hybrid (silicone) Slightly modified natural (dyed wool)	Synthetic Semi-synthetic Copolymers Composites, essential synthetic Tyre wear particles Modified natural (artificial NR, rayon)
<b>Solid state</b>	Polymer gels Fibres (wood/cellulose pulp) CNF, CNC (>100 nm)	Latex (binder, <1µm) Crystalline fibres of polymers, not formed by flow (modified natural fibres)	Solid ( $T_m/T_g >20^{\circ}C$ ) Laminate layers, structural element/composite
<b>Solubility</b>	Soluble polymers		Insoluble (1g dm <sup>3</sup> at 20°C)

Furthermore, synthetic polymers can be defined according the polymerisation reaction they are produced with: i.e. the addition or condensation of polymerisation. Similarly, semi-synthetic polymers are polymers made by treating a natural polymer chemically.

### Molar weight adjustment

The definition related to molar weight causes several uncertainties. One example is rayon fibre, the origin of which is biological; that is, wood pulp that contains cellulose, which is oxidatively, enzymatically or by other means degraded to reduce its molar mass and which then undergoes xanthation by carbon di-sulphide, and finally undergoes wet spinning in sulphuric acid and regenerated back to cellulose fibre. Since its origin is biological and chemically modified, it is referred to as a semi-synthetic polymer, but simultaneously it is cellulose. Low molar mass cellulose is found in nature, e.g. in bagasse. Simultaneously regenerated cellulose, rayon or lyocell, has changes in the crystal structure and the chain conformation, turning to Cel-II instead of naturally-occurring Cel-I. Both, however, are biodegradable in home compost.

However, polysaccharides degrade by oxidative and hydrolytic processes in naturally-occurring reactions by means of several enzymes in their normal decay process, from the high molar weight of natural polymers to oligo sugars and various metabolic products thereof in microbial activity<sup>iii</sup>.

The same degradation is also valid for proteins, including material like keratin, silk, wool, etc. This means that molar weight-adjusted natural polymers, including dissolving pulp and hydrolysed starch, are naturally occurring. Dissolving pulp, when produced from wood, contains only minor amounts of hemicellulose, but this is also typical of naturally-occurring materials, e.g. cotton linter.

## Dispersion and emulsions

Latex is a stable dispersion (emulsion) of polymer microparticles in an aqueous medium. It is found in nature, but synthetic latexes can be made by polymerising a monomer such as styrene that has been emulsified with surfactants. Latex, when found in nature, is a milky fluid found in 10% of all flowering plants (angiosperms).<sup>iv</sup>

Natural latex is complex emulsion of proteins, alkaloids, starches, sugars, oils, tannins, resins and gums that coagulate on exposure to air<sup>v</sup>. The rubbery stage, useful in forming coatings or binding, refers to a glass transition temperature (T<sub>g</sub>) markedly below the freezing point of water. This differs for plastics in the solid stage, being T<sub>g</sub> >20°C, as referred to in the table above. Latex is found in nature, such as in caoutchouc or Indian rubber.

Natural rubber biodegradation is a slow process, and the growth of bacteria utilising rubber as a sole carbon source is also slow. Therefore, incubation periods extending over weeks or even months are required to obtain enough cell mass or degradation products of the polymers for further analysis<sup>vi</sup>.

It seems that stable emulsions of slow biodegrading polymer microparticles in an aqueous medium are not only synthetic but also naturally occurring.

## Nano- and microparticles

A nanoparticle or ultrafine particle is usually defined as a particle of matter that is between 1 and 100 nanometres (nm) in diameter. The term is sometimes used for larger particles, up to 500 nm, or fibres and tubes that are less than 100 nm in only two directions. Their reactivity, toughness and other properties are also dependent on their unique size, shape and structure<sup>vii</sup>.

Even though cellulose is generally considered to be an environmentally-friendly material given its omnipresence in wood, fibres and tunicate animals, nanocellulose is both physically and chemically very different. These differences mean that it cannot be assumed that nanocellulose is as biodegradable and environmentally benign as cellulose in its native state. A range of nanocelluloses were synthesised, each with unique surface properties: TEMPO, HCl hydrolysed, sulphuric acid hydrolysed, cationic, and Jeffamine-treated. This was most apparent when comparing the TEMPO nanocellulose, which did not carry any functional groups, with microcrystalline cellulose. An early research project examined the biodegradability of nanocellulose and the effect of functional groups. It provides an important proof-of-concept, indicating that nanocellulose does biodegrade differently to natural celluloses<sup>viii</sup>.

Cellulose nanomaterials have unique properties that mean they have numerous potential applications. One of their most promising applications is transparent cellulose films with excellent strength, density and smoothness. Cellulose films could be utilised as gas barriers in packaging, substrates for printed electronics, in diagnostics or even as electronic displays instead of oil-based plastic films. From the safety point of view, the advantages of cellulose nanomaterials have been argued to be their benign nature towards humans and the environment as well as their biodegradability. However, when used in products, the biodegradability of cellulose nanomaterials might differ from that of pure materials. For example, during film preparation, the hydroxyl groups in the surface of cellulose nanofibrils form strong hydrogen bonds, which could make it more resistant to degradation upon drying of the film. Results on the biodegradability of different grades

of cellulose nanofibrils (CNF) and their products, namely CNF films and papers coated with CNF, are presented in this paper. In addition, results on the toxicity of cellulose nanofibrils to humans as well as ecotoxicity during biodegradation in the composting environment are reported. The results of biodegradability tests (OECD 301B) of two different grades of CNF indicate that their biodegradability is dependent on the fibrillation degree, with the finer grade degrading faster than the coarser grade. The biodegradability test (EN 14046) of CNF films and papers containing CNF showed that all the CNF products tested were biodegradable according to the requirements set in the standard (EN 13432). In the composting test (EN 14045), disintegration of CNF products was observed in the composting environment with no acute ecotoxicity during biodegradation. Regarding toxicity to humans, some indication of cytotoxicity was observed for nanoscale cellulose fibrils. However, all the other toxicity tests results, including in vivo tests with Nematode, showed no sign of toxicity [Heli Kangas, 2015 TAPPI International Conference on Nanotechnology for Renewable Materials Proceedings].

These examples indicate that nano-, micro- and macroparticles cannot be treated as a one homogeneous group of materials, but more individual cases differentiated by multiple aspects, including specific properties of base material, shape, surface activity and behaviour in its intermediator.

## Biodegradability

Regenerated cellulose films with water-repellent coatings, e.g. with plant oils, showed biodegradability in the soil and that viscosity average molecular weight  $M_{\eta}$ , tensile strength  $\sigma_b$  and the weight of the degraded films decreased sharply with the progress of degradation time, and the kinetics of decay were discussed. The degradation half-lives  $t_{1/2}$  of the films in soil at 10-20°C were given to be 30-42 days, and after two months the films were decomposed into CO<sub>2</sub> and water [Ind. Eng. Chem. Res. 1996, 35, 4682-4685]. Simultaneously, however, certain coatings used in cellophane are non-degradable like nitrocellulose-or PVdC-coated and may increase degradation times manyfolds<sup>ix</sup>.

One study investigated the enzymatical degradability and pilot-scale composting of 14 cellulose-based materials. The materials analysed here were cellulose regenerated from ionic liquid (EMIM[OAc]), carboxymethyl cellulose (CMC) crosslinked by aluminium salt (Al-salt), methyl cellulose, cellulose acetate, butylated hemicellulose: DS: 1, DS: 0.4, and DS: 0.2, cellophane, wet strength paper, nanocellulose, paper partially dissolved by IL, cellulose carbamate, cellulose palmitate and cellulose octanoate. The aim of the study was to show how chemical substituting and the substituent itself influence the biodegradability of cellulose materials. The enzymatic degradation and pilot-scale composting of these films shows the correlation between the hydrolysis rate and degree of substitution. The enzymatic hydrolysis of cellulose-based films decreased exponentially as the degree of substitution increased.<sup>x</sup>

Many different results in composting have been reported for cellulose acetate. Typical cigarette filter CA has degree of substitution  $ds < 2.5$  and is barely home compost degradable, but less substituted  $ds < 0.78$  grade is compostable.<sup>xi</sup> In addition, carboxy methyl cellulose CMC, with a degree of substitution (DS) of 0.7, was hydrolysed with a single endoglucanases enzyme until no further hydrolysis was observed. The hydrolysates were analysed for production of substituted and non-substituted oligosaccharides<sup>xii</sup>.

It can be concluded that for the chemical modification of semi synthetic polymer as such, it is not the denaturation but the degree of substitution that is essential for compostability, soil and sea degradability.



## Comparison of paper versus plastic

Both plastic and paper are valuable materials for several applications, especially in packaging. There are established recycling systems for both materials. The main differences between plastic and paper are as follows:

1. Paper is repulpable and plastic is remouldable, which means two different recycling systems.
2. Paper is essentially naturally occurring and plastic is synthetic fossil-based or occasionally bio-based.
3. Paper material is fully or dominantly soil- and aquatics-degradable, while plastic is optionally industrially compostable.

There are several product applications where the materials can be utilised as alternatives or side-by-side. Further, they have synergies in several products. The main common fields are found in packaging, and increasingly in appliances and construction.

	<b>Textile, non-woven</b>	<b>Paper</b>	<b>Laminate (laminated board)</b>	<b>Plastic</b>
Chemical composition	Crystalline fibres of polymers (textile)  Synthetic  Semi-synthetic  Binders (optional, latex)  Composites, essential synthetic  Slightly modified natural (optional)	Fibre (pulp) Wood-based pulp (mechanical, cellulose)  Agri pulp (straw, cotton, hemp) Inorganic filler (carbonate, clay, talk) Organic (starch, modified starch, micro and nanocellulose)	Composites, partially synthetic  Fibre (pulp) Wood-based pulp (mechanical, cellulose) Agri pulp (straw, cotton, hemp)  Inorganic filler (carbonate, clay, talk) Organic (starch, modified starch, micro and nanocellulose)	Synthetic  Semi-synthetic  Copolymers Composites, essential synthetic
Solid state	Structural (nonwoven, knitted, woven) Chemically bonded (latex) Thermally bonded (welded) Mechanically bonded (needed)	<b>Essentially naturally occurring</b> Structural (fibre web, hydroentangled) Fibre web (hydroentangled) Dispersion coated (optional)	<b>Essentially naturally occurring</b> <b>Layered (layered structural element)</b>  Multilayer Structural (fibre web, hydroentangled) Fibre web (hydroentangled)	Solid  Film, moulding  Multilayered (optional)
Solubility	Unpulpable	<b>Repulpable (in water)</b>	<b>Repulpable (in water)</b>	Non soluble
Substance	Mechanically openable (optional guarding)  Substances or mixtures containing microplastic (latex) is contained by technical means to prevent releases to the environment during end use, or  microplastics where microplastics are permanently incorporated into a solid matrix during end use.	Hydroentanglement (disintegrates in water) Substances or mixtures containing microplastic (latex) is contained by technical means to prevent releases to the environment during end use, or microplastics where microplastics are permanently incorporated into a solid matrix during end use.	<b>Disintegrates in vigorous pulper</b>  Substances or mixtures containing microplastic (latex) is contained by technical means to prevent releases to the environment during end use, or microplastics where microplastics are permanently incorporated into a solid matrix during end use.	Forming microplastics when deteriorates
Article	Disposable	<b>Recyclable</b>	<b>Recyclable</b>	Recyclable, reusable

Manufacturing methods differ from each other markedly, because the main feature of plastic is that it can be melted and moulded. Paper-converting technologies include dispersion coating, fibre casting and gluing, while plastic converting technologies are extrusion, moulding and fusing/welding. Extrusion coating and lamination, as well as several cutting, folding and bending technologies, are common for both and especially when in web converting.

How professionals and laymen understand plastic differs markedly, but the main issues are transparency, solid consistency as well as behaviour such as whether it disintegrates in water and whether it melts or not. This also leads to understanding that the behavioural differences in terms of water disintegration (repulpability) and meltability are the main differences.

## Options to replace essential synthetic polymers in papermaking with naturally-occurring polymers

### Polymers in papermaking

#### Wet-strength additives

Wet-strength additives ensure that paper retains its strength when it gets wet. This is especially important in tissue paper. Chemicals typically used for this purpose include epichlorohydrin, melamine, urea formaldehyde and polyimines. These substances polymerise in the paper and result in the construction of a strengthening network.

To enhance the paper's strength, cationic starch is added to wet pulp in the manufacturing process. Starch has a similar chemical structure to the cellulose fibre of the pulp, and the surface of both the starch and fibre are negatively charged. By adding cationic (positive-charged) starch, the fibre can bind with the starch and thus also increase the interconnections between the fibres. The positively-charged portion of the starch is usually formed by quaternary ammonium cations. Quaternary salts that are used include 2,3-epoxy propyl trimethyl ammonium chloride (EPTAC, also known as Glytac Quab, GMAC™) and (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC, also known as Quat 188, Quab 188, Reagens™).

#### Dry-strength additives

Dry-strength additives, or dry-strengthening agents, are chemicals that improve paper strength in normal conditions. These improve the paper's compression strength, bursting strength, tensile breaking strength, and delamination resistance. Typical chemicals used include cationic starch and polyacrylamide (PAM) derivatives. These substances work by binding fibres, often with the aid of aluminium ions in paper sheets.

#### Binders

Binders promote the binding of pigment particles between themselves and the coating layer of the paper. Common binders are styrene maleic anhydride copolymer or styrene-acrylate copolymer. The surface chemical composition is differentiated by the adsorption of acrylic acid or an anionic surfactant, both of which are used for stabilisation of the dispersion in water. Co-binders, or thickeners, are generally water-soluble polymers that influence the paper's colour viscosity, water retention, sizing and gloss. Some common examples are carboxymethyl cellulose (CMC), cationic and anionic hydroxyethyl cellulose (EHEC), modified starch and dextrin. Styrene butadiene latex, Styrene acrylic, dextrin and oxidised starch are used in coatings to bind the filler to the paper. Co-binders are natural products such as starch and CMC (Carboxymethyl cellulose) that are used along with synthetic binders, like styrene acrylic or styrene butadiene. Co-binders are used to reduce the cost of the synthetic binder and improve the water retention and rheology of the coating.

## Retention agent

A retention agent is added to bind fillers to the paper. Fillers, such as calcium carbonate, usually have a weak surface charge. The retention agent is a polymer with high-cationic, positively-charged groups. An additional feature of a retention agent is to accelerate the dewatering in the wire section of the paper machine. Polyethyleneimine and polyacrylamide are examples of chemicals used in this process.

## Paper converting

### Dispersion coating

Barrier polymer dispersion coating is understood to mean the coating technique where latex, like styrene acrylic or styrene butadiene, dextrin or oxidised starch, which are used to bind the filler and co-binders, which are natural products such as starch and CMC (carboxymethyl cellulose), is applied to the surface of paper or board as such to form a solid, non-porous film after drying. The target of dispersion coating is to achieve a barrier layer against water, water vapour, grease, oil or gas with a coating that is readily removable in repulping during the recirculation of fibres.

### Lamination

Lamination is the technique/process of manufacturing a material in multiple layers, so that the composite material achieves improved strength, stability, sound insulation, appearance or other properties from the use of the differing materials, such as plastic, polyethylene, polypropylene, polyester as well as biodegradable alternatives like polylactic acid. A laminate is a permanently assembled object created using heat, pressure, welding or gluing.

## Naturally-occurring polymeric materials

*'Substances that occur in nature means a naturally-occurring substance as such, unprocessed or processed only by manual, mechanical or gravitational means, by dissolution in water, by flotation, by extraction with water, by steam distillation or by heating solely to remove water, or which is extracted from air by any means.'*

There are many naturally-occurring polymeric materials. Many are quite complex. It is possible, however, to apply an arbitrary classification and to divide them into six main categories.<sup>xiii</sup> These are:

1. Polysaccharides. This category includes starch, cellulose, chitin, pectin, alginic acid, natural gums and others. A list of polysaccharides from varying sources is given below:
  - a. Examples of polysaccharides from higher plants include starch, cellulose and exudate gums like arabinogalactan, guar gum and gum arabic.
  - b. Examples of algal polysaccharides: alginates, galactans and carrageenan.
  - c. Examples of polysaccharides from animals: chitin, chitosan, glycosaminoglycans (GAGs) and hyaluronic acid (HA).
  - d. Examples of polysaccharides from microorganisms: dextran, gellan gum, pullulan, xanthan gum and bacterial cellulose.

2. Proteins or naturally-occurring polyamides found in animal and vegetable sources.
  - a. Animal-based proteins with nutritional value, casein from milk, gelatin from e.g. pig skin, collagen from bones and connective tissues, and egg white
  - b. Animal-based proteins without marked nutrition value, like fibrions including silk, keratin, elastin and resilin.
  - c. Plant-based protein, such as those from whey and soy.
3. Polyisoprenes or natural rubbers and similar materials that are isolated from saps of plants.
  - a. Natural rubber, *caucho*, consists of polymers of the organic compound isoprene, with minor impurities of other organic compounds, plus water, harvested mainly in the form of latex from the rubber tree or others.
  - b. Some plants that have been considered as alternative rubber sources are guayule, Russian dandelion, rubber rabbit brush, goldenrod, sunflower, fig tree and lettuce. Two of these plants seem to be the best alternatives to *Hevea brasiliensis*: guayule and Russian dandelion.
4. Polynucleotides include all the DNAs and all the RNAs found in all living organisms.
5. Lignin or polymeric materials of coniferyl alcohol and related substances.
6. Naturally-occurring miscellaneous polymers, such as shellac, a resin secreted by the lac insect. This is a complex cross-linked polyester of 9,10,16-trihydroxy-exadecanoic acid (aleuritic acid).
7. Waxes are synthesised by many plants and animals.
  - a. Those of animal origin typically consist of wax esters derived from a variety of fatty acids and carboxylic alcohols. In waxes of plant origin, characteristic mixtures of unesterified hydrocarbons may predominate over esters.
    - i. Beeswax is myricyl palmitate, which is an ester of triacontanol and palmitic acid.
    - ii. Spermaceti occurs in large amounts in the head oil of the sperm whale. One of its main constituents is cetyl palmitate, another ester of a fatty acid and a fatty alcohol.
    - iii. Lanolin is a wax obtained from wool, consisting of esters of sterols
  - b. Plants secrete waxes into and on the surface of their cuticles as a way to control evaporation, wettability and hydration. The epicuticular waxes of plants are mixtures of substituted long-chain aliphatic hydrocarbons, containing alkanes, alkyl esters, fatty acids, primary and secondary alcohols, diols, ketones and aldehydes.
    - i. From a commercial perspective, the most important plant wax is carnauba wax, a hard wax obtained from the Brazilian palm *Copernicia prunifera*. Containing the ester myricyl cerotate, it has many applications, such as confectionery and other food coatings, car and furniture polish, floss coating and surfboard wax.
    - ii. Other more specialised vegetable waxes include jojoba oil, candelilla wax and ouricury wax.

## Valorisation of changeability

### Guar gum, carrageenan

When making paper from an aqueous paper making stock, a binder comprising colloidal silicic acid and guar gum is added to the stock to improve the paper or the retention of the stock components so that the pollution problems and the amount of valuable substances in the white water are reduced. However, it does not necessarily perform as such and as the only polymer. The guar gum is amphoteric or preferably cationic and may form part of the binder complex in a mixture with cationic starch. The weight ratio of guar gum to SiO<sub>2</sub> or of guar gum plus cationic starch to SiO<sub>2</sub> is between 0.1:1 and 25:1.<sup>xiv</sup>

Carrageenan also requires additional chemicals to be effective. Carrageenans are commercially important sulphated gums found in various species of red seaweeds (Rhodophyta), wherein they serve a structural function similar to that of pectins in land plants. In this study, carrageenan was used independently or in combination with cationic polyacrylamide (CPAM) and/or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> to explore its application as a dry strength additive in papermaking xv.

### Bacterial, nano- and micro-fibrillated cellulose

The term *nanocellulose* refers to cellulosic materials having at least one of their dimensions on the nanometer scale. Nanocelluloses can be produced by different methods and from various lignocellulosic sources. There are both chemical and mechanical methods for producing CNC and CNF from cellulose, which may mean that also CNF does not occur naturally.

Applications of nanocellulose in papermaking include increased tensile and burst strengths, weight loss, improved barrier properties for oils, oxygen and moisture, better printing surface, and so on.<sup>xvi</sup>

Bacterial nanocellulose (BNC) is a unique natural nanomaterial that shares very few similarities with other natural or industrially-produced nanomaterials. BNC can be produced by a variety of bacteria as a survival aid in different ecological niches. BNC is traditionally produced by static or shaking culture methods, and the 'mother vinegar', or biofilm, is a typical example of this product after static vinegar fermentation. BNC has great potential in biomedicine, and recent studies have also demonstrated its use in the papermaking industry. It has nanoscale fibre size and large numbers of free hydroxyl groups, which ensure high inter-fibre hydrogen bonding. Thus, BNC has great potential as a reinforcing material, and is especially applicable for recycled paper and for paper made of non-woody cellulose fibre. As well as enhancing the strength and durability of paper, modified BNC shows great potential for the production of fire resistant and specialised papers. However, the biotechnological aspects of BNC need to be improved to minimise the cost of its production, and to thus make this process economically feasible.<sup>xvii</sup>

### Dextrin

Hydrophobic starches are not yet widely used in papermaking. A low-viscosity dextrin is used in Europe as a total chlorine-free (TCF) coating binder.<sup>xviii</sup> However, dextrin is typically used with other functional polymers.<sup>xix</sup>

### Natural rubber latex, *caucho*

Although there are something like 200 plants in the world that produce latex, over 99 per cent of the world's natural rubber is made from the latex that comes from a tree species called *Hevea brasiliensis*, widely known as the rubber tree. These trees are grown on large plantations, primarily found in Thailand, Indonesia, Malaysia and Liberia.

This latex is about one-third water and one-third rubber particles held in a form known as a colloidal suspension. Natural rubber is a polymer of isoprene (also known as 2-methylbuta-1,3-diene) with the chemical formula  $(C_5H_8)_n$ . To put it more simply, it is made of many thousands of basic  $C_5H_8$  units (the monomer of isoprene) loosely joined to make long, tangled chains. The polymers are not biodegradable as the composability requires.

Caucho latexes are not applied in papermaking due to the markedly better control of properties affecting processability and especially the end properties of the coated paper and board.

### **Materials that cannot be replaced**

Polyethylenimine (PEI) or polyaziridine is a polymer with a repeating unit composed of the amine group and two carbon aliphatic  $CH_2CH_2$  spacers. Linear polyethyleneimines contain all secondary amines, in contrast to branched PEIs which contain primary, secondary and tertiary amino groups. Totally branched, dendrimeric forms were also reported. PEI is produced on an industrial scale and has many applications, which are usually derived from its polycationic character.

Polyethyleneimine has many applications in products such as detergents, adhesives, water treatment agents and cosmetics. Owing to its ability to modify the surface of cellulose fibres, PEI is employed as a wet-strength agent in the papermaking process. It is also used as flocculating agent with silica sols and as a chelating agent with the ability to complex metal ions. However, PEI is not biodegradable, it has a number of uses in laboratory biology, especially tissue culture, but is also toxic to cells if used in excess.

### **Polyacrylamide**

**Polyacrylamide** (PAM) is a commercially relevant cationic polymer utilised mainly for water treatment due to its high efficiency and rapid dissolution. One of the most widespread uses for polyacrylamide is to flocculate solids in a liquid. This process applies to water treatment, and processes like papermaking and screen printing.

PAM as polymeric soil conditioning material was published especially as linear, water-soluble, anionic polyacrylamide. PAM is relatively non-toxic to humans, animals, fish and plants, but not biodegradable.<sup>xx</sup>

### **Styrene acrylic or styrene butadiene latex**

The benefits of the co-polymerised styrene-butadiene latex are many, including filler acceptance and tensile/elongation balance. The flexibility of this co-polymer allows for a near-infinite number of mixtures that result in high water resistance and adhesion to challenging substrates. These qualities of styrene-butadiene latex make this synthetic latex essential to an ever-widening group of markets, including adhesives, paints and coatings, packaging, nonwovens and textiles, paper and construction.

Function	Synthetic	Modified natural polymers	Optional naturally-occurring replacement	
Wet-strength additives	polyimides	cationic starch	non-existent	
Dry-strength additives	polyacrylamide (PAM)	cationic starch	guar gum, bacterial cellulose, nano- and micro-fibrillated cellulose	
Binders	styrene maleic anhydride copolymer or styrene-acrylate copolymer	carboxymethyl cellulose (CMC), cationic and anionic hydroxyethyl cellulose (EHEC), modified starch	dextrin	
Retention agent	polyethyleneimine, polyacrylamide		non-existent	
Dispersion coating	styrene acrylic or styrene butadiene latex	Co-binders: dextrin, oxidised starch to bind the filler and co-binders are natural products such as starch and carboxymethyl cellulose (CMC)	Natural rubber latex, <i>caucho</i> (alternative rubber sources include <i>quayule</i> )	
Lamination	polyethylene, polypropylene, polyester	polylactic acid	non-existent	

## Conclusion

Contemporary papermaking would not be possible industrially without synthetic and modified natural polymers like modified starch, especially cationic and oxidised starch, as well as carboxymethyl cellulose (CMC), cationic and anionic hydroxyethyl cellulose.

## Contradiction in definitions

Defining modified natural polymers in all cases as a plastic is problematic on occasion. For example, carboxymethyl cellulose CMC is used in food under the E-numbers E466 or E469 (when it is enzymatically hydrolysed) as a viscosity modifier or thickener, and to stabilise emulsions in various products including ice cream. It is also a constituent of many non-food products, such as toothpaste, laxatives, diet pills, water-based paints, detergents, textile sizing, reusable heat packs and various paper products. It is used primarily because it has high viscosity, is non-toxic, and is generally considered to be hypoallergenic as its major source of fibre is either softwood pulp or cotton linter. CMC is used extensively in gluten-free and reduced-fat food products. In laundry detergents, it is used as a soil suspension polymer designed to deposit onto cotton and other cellulosic fabrics, creating a negatively-charged barrier to soils in the wash solution.

Gelatin is a very attractive biopolymer for food packaging applications because it is a renewable material, and it has a relatively low price. It has achieved acceptance as a 'Generally Recognized as Safe' (GRAS) substance in the area of food additives by the US Food and Drug Administration (FDA), and has excellent film-forming ability, gel-forming properties at temperatures of around 35°C, excellent versatility due to its  $\alpha$ -amino acid composition, abundance, low cost and biodegradability. These features make gelatin an attractive protein in the design and development of functional films with potential applications in the food sector. However, these beneficial characteristics are counterbalanced by the hydrophilic nature of gelatin, which imparts high moisture sensitivity to the derived films compromising their broader application. Numerous attempts have been undertaken to improve and modulate gelatin film properties to achieve comparable performance to that of the conventional non-biodegradable plastics used in food packaging, including chemical, physical and enzymatic cross-linking, plasticising, compounding with other polymers, laminating and reinforcing with micro- and nano-size reinforcements. All these strategies offer the possibility to be incorporated to obtain a very wide range of tailor-made materials.<sup>xxi</sup>

Therefore, ice cream cones and many other applications would be classified as plastic, if the definition of plastics were to be changed in EU legislation. It is a single-use food packaging intended for initial use. In addition, gelatin, a hydrolysed collagen, would no longer be an additive E441 but an ingredient, which would mean that marshmallows and wine gums would also be classified as plastic.



- 
- <sup>i</sup> Environmental Hazards of Plastic-Coated Paper Products, Eco-Cycle, [https://www.ecocycle.org/files/pdfs/microplastics\\_in\\_compost\\_summary.pdf](https://www.ecocycle.org/files/pdfs/microplastics_in_compost_summary.pdf)
- <sup>ii</sup> Microplastics Occurrence, the effects and sources of releases into the environment in Denmark. Environmental project No. 1793, 2015. <https://www2.mst.dk/Udgiv/publications/2015/10/978-87-93352-80-3.pdf>
- <sup>iii</sup> Stone B., Svensson B., Collins M., Rastall R. (2008) Polysaccharide Degradation. In: Fraser-Reid B.O., Tatsuta K., Thiem J. (eds) *Glycoscience*. Springer: Berlin, Heidelberg
- <sup>iv</sup> Anurag A. Agrawal; d Kotaro Konno (2009). 'Latex: a model for understanding mechanisms, ecology, and evolution of plant defense against herbivory'. *Annual Review of Ecology, Evolution, and Systematics*. **40**: 311–331
- <sup>v</sup> Paul G. Mahlberg (1993). 'Laticifers: an historical perspective'. *The Botanical Review*. **59** (1): 1–23
- <sup>vi</sup> *Applied and Environmental Microbiology*, June 2005, p. 2803–2812
- <sup>vii</sup> *Arabian Journal of Chemistry* (2019) 12, 908-31
- <sup>viii</sup> <https://grantome.com/grant/NSF/CBET-1236005>. However, in later studies it has been shown that nanocellulose is biodegradable [*Progress in Polymer Science* 87 (2018) 197-227]
- <sup>ix</sup> *J Polym Environ* (2015) 23:449–458 DOI 10.1007/s10924-015-0740-9
- <sup>x</sup> *Journal of Polymers and the Environment*, (2019) 28, 458-470
- <sup>xi</sup> *Microbiology of composting*, Springer 2013, p.273-286
- <sup>xii</sup> *Biopolymers*, 2002 Jan; 63(1):32-40
- <sup>xiii</sup> [link.springer.com/chapter/10.1007/978-1-4615-4227-8\\_7](link.springer.com/chapter/10.1007/978-1-4615-4227-8_7)
- <sup>xiv</sup> <https://patents.google.com/patent/US4755259A/en>
- <sup>xv</sup> <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5295721/>
- <sup>xvi</sup> [https://link.springer.com/chapter/10.1007/978-3-030-05399-4\\_36](https://link.springer.com/chapter/10.1007/978-3-030-05399-4_36)
- <sup>xvii</sup> <https://link.springer.com/article/10.1007/s10570-019-02566-y>
- <sup>xviii</sup> James N. BeMiller, Roy L. Whistler - 2009 - *Technology & Engineering*, p.665
- <sup>xix</sup> *Palpu Chongi Gisul/Journal of Korea Technical Association of the Pulp and Paper Industry* 49(2):13-22 · March 2017
- <sup>xx</sup> <https://www.nature.com/articles/s41545-018-0016-8>
- <sup>xxi</sup> [https://www.researchgate.net/publication/236111183\\_Gelatin\\_Films\\_Renewable\\_Resource\\_for\\_Food\\_Pack\\_aging](https://www.researchgate.net/publication/236111183_Gelatin_Films_Renewable_Resource_for_Food_Pack_aging)

NOTE: A correction has been made to clarify the IUPAC definition to page 4 on 28<sup>th</sup> September, 2020: According to the IUPAC definition, plastics are expressed in ISO 472:2003 as *mixtures comprising essentially of high molar weight polymer, which are shaped by flow at some stage of their manufacturing.*