



Review

Degradable or not? Cellulose acetate as a model for complicated interplay between structure, environment and degradation

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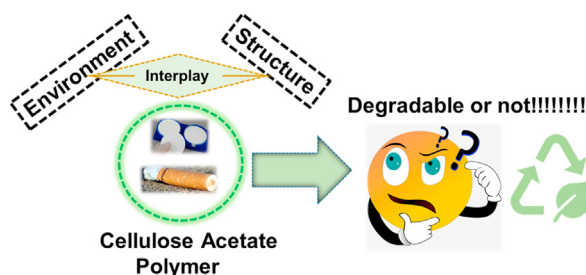
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HIGHLIGHTS

- Chemical modification affects degradability of natural polymers.
- Biodegradability of cellulose acetate largely depends on the degree of acetylation.
- Other material modifications can enhance or further limit the degradability.
- Degradation rate is also highly influenced by the actual degradation environment.

GRAPHICAL ABSTRACT



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ABSTRACT

Degradable and/or biobased plastics are advocated as possible solution to plastic waste problem. Although mechanical and chemical recycling or energy recovery are in many cases a preferred option to regain the material value, for some applications composting is ideal. However, to more generally ensure complete degradation of plastics within a relatively short time-frame in all-natural environments would be extremely challenging, if not impossible. It is also important to keep in mind that it is the chemical structure and composition in combination with degradation environment that determines whether the plastic will degrade and within what timeframe. Biobased materials can be as stable as the petroleum-based counterparts and face the same waste-management problems. One interesting group of biobased materials are the modified biopolymer-based plastics, such as cellulose acetate (CA). How different modifications affect the inherent degradability of biopolymers is still poorly understood, which is reflected in the contradictory literature. This mirrors the complex interplay between structure-environment-degradability, where structural changes such as degree of substitution in the case of CA and changes in selected degradation environment can lead to totally different end-results and conclusions. Understanding these interactions is a fascinating scientific question. The deposition of CA based products as common surface litter makes it also question of societal and environmental interest. The purpose of this review is to summarize the existing knowledge on degradation of CA and in larger perspective highlight the complicated nature of plastic and bioplastic degradation in natural environments and the interplay between different environmental parameters and material modifications on this process.

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Contents

1. Introduction	2
2. Factors affecting the CA degradation	3
3. Degradation of CA in simulated, accelerated or natural environments	3
3.1. Chemical hydrolysis of CA	4
3.2. Biodegradation of CA by specified microorganism and enzymes	4
3.3. Degradation of CA in complex environments	4
3.4. The influence of UV irradiation on CA	5
4. The effect of material modifications on the degradation process	5
4.1. Chemical functionalization	5
4.2. Additives that enhance photodegradation	6
4.3. Addition of plasticizers, water-soluble adhesives or polymers	6
4.4. Alterations in design and fabrication processes	6
5. The case of cigarette butts	6
6. Summary and future outlook	7
CRediT authorship contribution statement	7
Declaration of competing interest	7
Acknowledgments	7
References	7

1. Introduction

The accumulation of huge piles of plastic waste in landfills and natural environments, especially in the sea and coastal regions, is one of the largest environmental concerns facing us. The very slow degradation of plastic waste under natural environmental conditions calls for immediate action. However, there is no one solution that can take care of the whole plastic waste problem. For many plastics recycling to new materials, new chemicals or energy is a viable and preferred option. However, material recycling is a complicated process due to logistics of waste collection, separation, transportation, large variety of plastic types and properties, states of degradation, additive packages, multicomponent products and possible contamination of materials. Furthermore, the current processes are often energy- and resource-intensive.

In other cases, degradable material can be a preferred choice due to degradation being part of the function, due to high risk for the product to end up in the surroundings or contamination by organic matter such as food residues (Albertsson and Hakkarainen, 2017; Shen et al., 2020). The materials, where degradability is part of the function are more easily achieved as they can be designed for specific disposal route or degradation environment with relatively well-defined and established conditions. For example, a plastic bag for garden waste or food waste can be designed to be degradable in compost by combined action of heat, moisture and bacteria, while mulching film should be degraded by sunlight, heat, moisture and soil bacteria. Already here the environmental parameters have much larger variance depending on e.g. location and weather condition during the specific year.

Throwing plastic products in the nature is not a waste management option, but some products, like cigarette butts (CB) or fishing nets have high risk of ending up in the nature and could with benefit be designed for enhanced degradability. To ensure complete degradation within a relatively short time-frame is, however, extremely challenging, if not impossible, due to the large variation of natural environments, including the type of environment, location and season. One polymer structure can be rapidly degradable in sunlight while being persistent to moisture and the opposite. Furthermore, the materials susceptibility to degradation is highly influenced by its physical and chemical structure,

composition and even macroscopic size and shape. Even a small modification can significantly affect the degradation potential in specific environment. A further complication is the concept of degradation or biodegradation, what is reported as degradation is sometimes just growth of microorganism on the surface or weight loss due to leaching of additives or low molar mass part of the material and not true or at least not complete degradation of the polymer (Zumstein et al., 2019). It is imperative to try to understand these factors and their complicated interplays, which can drive and accelerate or prevent the degradation of plastics and bioplastics in natural environments (Puls et al., 2011).

Cellulose acetate (CA) is widely used chemically modified natural polymer, that is considered as semi-synthetic polymer. Its applications vary from textile industry to plastic films, packaging, and cigarette filter tows (Pauly et al., 1995). It is an eco-friendly material and majorly sourced from cellulose present in wood or cotton linters through reaction with acetic acid. Cellulose is a natural biopolymer and inherently degradable in suitable natural environments. The literature on degradation of CA in different environments, on the other hand, is contradictory due to the complex interplay between structure-environment-degradability as described above. It is of high scientific interest to understand the prerequisites for environmental degradability of modified biopolymers. Furthermore, the disposition of CA based products as common surface litter, especially in the form of cigarette butts, makes it also a question of high societal and environmental interest. This understanding is the key for developing strategies and materials that have the pre-requisites to degrade within relatively short time-frame under different environmentally relevant conditions. The purpose of the review is to present an overview of existing knowledge, evidences and reports on degradation of CA polymers under different environmentally relevant parameters and in larger perspective to create awareness concerning the complicated nature of plastic and bioplastic degradation in natural environments and the influence of different material modifications on this process. As the concept is challenging, it is crucial to understand the sensitivity of the degradation process in simulated or real natural environments and its control by structure-environment-degradation relationships (Glasser, 2004). This awareness and understanding is even more critical as the interest towards

“degradable” materials is increasing and we in larger scale proceed from petroleum-based to biobased materials.

2. Factors affecting the CA degradation

CA is produced from cellulose through acetylation of some of the hydroxyl groups. The favourable properties of CA include hardness, good impact resistance, optical transparency, resistance to hydrocarbons and lack of static electricity (Ach, 1993; Quintana et al., 2014). According to existing literature CA is potentially biodegradable (Komarek et al., 1993; Buchanan et al., 1993). However, the biodegradation rate is governed by the degree of acetyl-substitution (DS) and the actual conditions the material is subjected to (Chandra and Rustgi, 1998). The biodegradation rate decreases as the function of increasing DS (Samios et al., 1997; Ross et al., 2017). In addition to DS, molar mass, crystallinity, physical form, the presence of contaminants and electron acceptors have been reported to control the degradation rate (Abrusci et al., 2009). Numerous “environmental factors” (see Fig. 1) in combination with the structural features further influence the degradation rate at any given location, including: temperature, humidity, pH, sunlight and availability of oxygen, nutrients and microorganisms (Laycock et al., 2017). An environment that can partially deacetylate CA with high DS has generally been identified as a pre-requisite for further biodegradation (Ho et al., 1983). This acetylation can be achieved chemically or by acetyl esterase enzymes. After complete or partial deacetylation, the degradation can proceed by chain scissions, which shortens the chain length and leads to weakened and

embrittled material and finally to production of sugars (Göpferich, 1996). The chain scission can be catalyzed by strong acids or in natural environments by enzymes including cellobiohydrolases and cellobiases (Klyosov, 1990).

Deacetylation is the rate determining step during biodegradation of CA. The almost simultaneous further degradation of the partially deacetylated chains or chain segments can lead to misinterpretation concerning the process, as the parallel processes can keep the DS value more or less constant. To understand the degradation process and how it is governed by complicated interdependencies, the ability to fully characterize the CA material and the changes taking place at molecular level is crucial. The differences in chemical structure including DS, crystallinity, molar mass and composition will affect the degradation process and ultimate fate of the material, which can without proper characterization lead to very different conclusions. While precise molecular level characterization of materials and their the degradation process is of interest to increase the scientific understanding on how polymer structure influences degradability in different environments, the claims of full biodegradability should be confirmed by measuring conversion to CO₂ or microbial biomass under standardized conditions for the specific environment (e.g. compost, soil, marine) (Zumstein et al., 2019).

3. Degradation of CA in simulated, accelerated or natural environments

The amount of plastics accumulating in the environment is

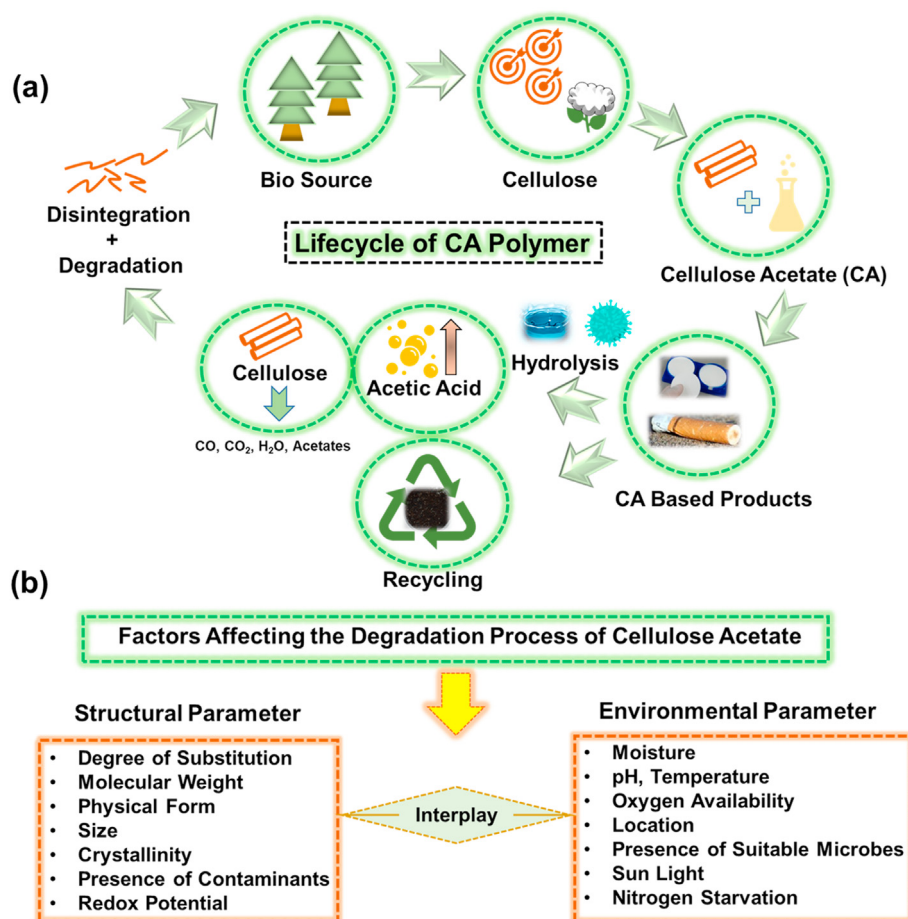


Fig. 1. (a) Possible lifecycle of CA polymers and (b) factors affecting the degradation process.

growing rapidly, yet our understanding of its persistence and potential time-scales for degradation are limited. Exposure to e.g. sunlight, mechanical wear due to wind or waves, lake-or seawater, soil, compost and micro-organisms causes chemical and physical changes in polymeric materials. These changes can with time be observed both at molecular level and at macroscopic level. Depending on the material and the exact exposure conditions, the time scale for observed changes can vary greatly. Simplified testing environments can be utilized for evaluation of selected factors on the degradation process and degradation rate (Fig. 2). These and the potential ways to accelerate the degradation process are further discussed in the following sections.

3.1. Chemical hydrolysis of CA

Chemical and biological hydrolysis are the principal mechanisms by which cellulose-based polymers degrade. As already stated above, concerning the “environmental degradation” of cellulose acetate with high DS, the hydrolysis of acetate groups is the first step required for further degradation to occur. Acetate groups are susceptible to chemical hydrolysis, but this process is slow in ambient conditions. The degradation process leading to release of acetic acid has been called the “vinegar syndrome” as it causes a vinegar-like odour. The chemical hydrolysis process can be catalyzed by strong acids (e.g. hydrochloric acid, *ortho*-phosphoric acid, sulfuric acid) and bases (e.g. sodium hydroxide) (Hosono et al., 2008; Yamashita and Endo 2004). As an example, incorporation of phosphoric acid in CA films accelerated the subsequent biodegradation rate of the films in soil (Yamashita and Endo, 2004). Based on above, different approaches to accelerate the biodegradation rate of CA polymers by chemically catalyzed hydrolysis of acetate groups have been proposed. For example, an acid compound with larger acid dissociation constant than that of acetic acid was added to CA materials to accelerate the subsequent biodegradation rate (Quintana et al., 2012). Another patented process incorporated a salt or ester of oxygen acid of phosphorus or carbonic acid and salt as “biodegradation promoting agents” for CA (Yamashita and Endo, 2004). An enhanced rate of hydrolysis was achieved by the in situ generation of a mineral acid or its salt such as sodium hydrogen sulfate ($pK_a = 1.9$) can be formed via hydrolysis from cellulose sulfate sodium salt or Vitamin C sulfate mono-sodium salt (L-ascorbic acid-2-sulfate mono-sodium salt) (Robertson et al., 2012).

3.2. Biodegradation of CA by specified microorganism and enzymes

Degradation of polymers in well-defined aqueous environment in laboratory environment is a relatively controlled process, although several mechanisms can act simultaneously (Laycock

et al., 2017). To be able to draw more general conclusions concerning the potential degradability, degradation mechanism versus environmental requirements for the changes to take place, the material and changes taking place in its chemical and physical structure need to be carefully characterized. In the case of CA for example differences in the DS of the materials has led to different conclusions concerning the degradability. A suitable combination of enzymes can significantly promote the degradation rate, e.g., CA degradation by cellulases is enhanced by combination with enzymes that are capable of deacetylation (Glasser et al., 1994; Altaner et al., 2003; Itävaara et al., 1999).

Around half of the studied cellulolytic bacteria could grow on cellobiose octaacetate model compound, however, very few could release detectable amounts of enzymes (Reese, 1957). Some of the studied bacteria also produced enzymes when grown on cellulose or water-soluble low DS CA (DS 0.76). In another study potent CA degrading microorganisms *Rhizobium meliloti* and *Alcaligenes xylosoxidans* caused 34% and 23% weight loss, respectively, of CA membrane after 150 days, which is still quite slow degradation rate. The fungi *Pestalotiopsis westerdijkii* QM 381 could release exocellular cellobiose octaacetatease (Gu et al., 1993). *P. westerdijkii* (containing cellulolytic and acetyl esterase components) and yeast were utilized to predigest water-soluble cellulose acetate (WSCA) (DS 0.4–0.8) to form reducing sugars and acetate prior to converting these intermediate products to ethanol (Downing et al., 1987). CA with DS values between 1.7 and 2.5 was biodegraded under aerobic conditions by an enrichment culture that was initiated with an activated sludge inoculum (Buchanan et al., 1993). The process started by partial deacetylation followed by depolymerisation.

Two bacteria strains of *Neisseria sicca* could degrade CA with a DS of 2.3 (Sakai et al., 1996). The authors explained this as combined action of esterases that deacetylated CA, followed by cellulases which cleaved the cellulose backbone into smaller fragments (Sakai et al., 1996). The highest degradation rates correlated to 60% and 45% weight loss within 20 days. In correlation, another study showed that for a successful enzyme-catalyzed reaction, a cocktail of enzymes, which could deacetylate and randomly cleave CA chains to generate shorter CA fragments, was the most suitable (Haske-Cornelius et al., 2017). However, it was also shown that when the DS was over 1.8, esterase enzymes could not efficiently attach to the cellulose surface and cleave the acetate bonds (Haske-Cornelius et al., 2017). Other studies also demonstrated decreasing biodegradation rate as function of increasing DS (Leppänen et al., 2020; Ho et al., 1983). The maximum DS for CA is 3 and common DS for commercial CA products, such as cigarette butts (CBs) is 2.5. An interesting study showed that regioselectively substituted CA degraded faster than randomly substituted CA with similar (Takeda et al., 2016). However, enzymatic degradation was only observed for CA with low DS. Neither regioselectively nor randomly substituted CA with $DS \geq 2$ was susceptible to enzymatic degradation by cellulase from *Toricoderma reesei*. This study further revealed, through analysis of the formed water-soluble products, that free hydroxyl groups at C6 position are important for enzymatic degradation of CA by *endo*-glucanases, cellulases that randomly cleave glycosyl bonds at the middle of cellulose chain. However, the enzymatic hydrolysis by cellobiohydraz, that cleaves glycosyl bonds starting from chain ends, was disturbed even by acetylation at C2 and C3.

3.3. Degradation of CA in complex environments

The prediction of degradation potential and degradation time is difficult in complex environments such as soil, seawater and compost as several degradation mechanisms may proceed

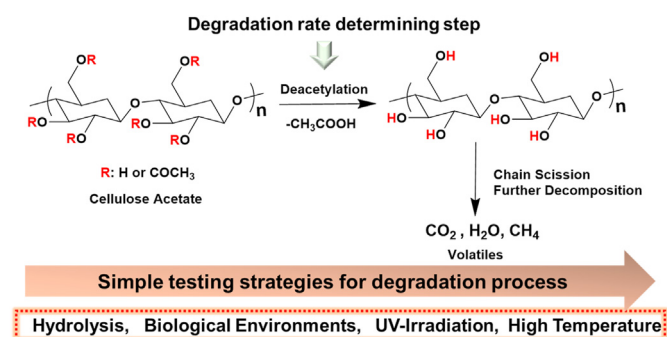


Fig. 2. The potential degradation pathway and simple testing strategies adopted for evaluating the degradation of CA.

simultaneously. The processes such as swelling, leaching, hydrolysis, oxidation, biodegradation and fragmentation may take place parallel to each other and the degradation in real natural environments is further influenced by season and location dependent variables such as humidity, temperature and sunlight (Laycock et al., 2017). Gu et al. investigated the biodegradability of CA films with DS values of 1.7 and 2.5 by aging the materials in-laboratory composting test vessels kept at -53°C (Gu et al., 1993, 1998). Authors proposed formation of low molar mass products through random chain scission. The degraded products were analysed by different techniques such as nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC) and size exclusion chromatography (SEC) to understand the degradation mechanism (Capitain et al., 2020; Gu et al., 1993). Further research by the same group also stated that water content in compost was important for the degradation rate (Gu et al., 1994). 45–50% of cellulose acetate powders with DS 1.5 and 2.5 were mineralized to CO_2 during 55 days of controlled composting. However, only 9% or 15% were mineralized when DS was increased to 3.0 or DS 2.5 granules were investigated instead of powder, respectively. The same materials were not biodegraded when subjected to aquatic Sturm test (Van der Zee et al., 1998). An interesting study performed on radiolabeled cellulose acetate subjected to mixed culture of microorganisms derived from activated sludge showed that 80% of CA with DS 1.85 could be biodegraded to $^{14}\text{CO}_2$ during 29 days. When DS was increased to 2.07 and 2.57, the biodegradation rate decreased to $\sim 60\%$ (Komarek et al., 1993).

Methyl cellulose with DS 1.7 was completely degraded during 12 weeks in pilot-scale compost, while cellulose acetate with high DS 2.5 showed negligible degradation (Leppänen et al., 2020). The degradation rate of cigarette filters made of cellulose and cellulose acetate illustrated significant differences when the two materials were buried in plastic containers containing compost (Joly and Coulis, 2018). Cellulose filter exhibited 64% weight loss during 157 days compared to only 17% weight loss for cellulose acetate. Both materials degraded slowly on the soil surface with only 5–10% weight loss. An important message from this study is that it takes time even for natural polymers, such as cellulose, to degrade and the rate is highly dependent on the environmental conditions. Cellulose acetate with DS 2.85 showed approximately 30% weight loss after 35 days of soil burial (Fei et al., 2015). However, the weight loss plateaued after 35 days and no significant further increase was observed up to end of the testing period of 120 days.

Blending of poly(butylene succinate) (PBS) with CA membrane significantly influenced the morphology and hydrophilicity and a sponge-like structure was formed in compost environment. These membranes showed weight loss up to 40% for the blend containing the highest amount of PBS (CA/PBS 30/70) (Ghaffarian et al., 2013), while the weight loss of 50/50 CA/PBS blend was only around 20%. These results strongly indicate that only or mostly PBS was degraded, which is further confirmed by the negligible weight loss for pure CA membrane.

3.4. The influence of UV irradiation on CA

Exposure to sunlight (UV irradiation) can largely affect the fate and degradation rate of plastics after disposal in landfills or in natural environment as long as the material remains on the surface accessible to sunlight (Ishigaki et al., 2002; Chamas et al., 2020). UV irradiation also generally enhances the biodegradability of plastics by introduction of polar groups and increase the surface area. The irradiation can also lead to chain scission, formation and leaching of low molar mass water-soluble compounds from the material, which can increase the accessibility to enzymes. The absorption maximum for cellulose acetate is at $\sim 260\text{ nm}$, while the cut off for

sunlight reaching earth is at 300 nm . This indicates that pure cellulose acetate might not be significantly degraded by natural sunlight. However, contaminants or additives (e.g. photocatalysts or photosensitizers) can act as chromophores and initiate photo-degradation of CA, which is discussed in more detail under 4.2.

One study investigated the effect of UV irradiation on subsequent enzymatic degradation. They reported that UV irradiation of CA with DS 2.5 did not cause significant changes to DS, but it significantly reduced the molar mass. Authors reported only 2.5% weight loss in the presence of cellulase enzymes without UV irradiation. This weight loss increased to 60% after UV irradiation, while 23% weight loss was observed for UV irradiated samples in sterilized acetate buffer solution without cellulase enzymes. (Ishigaki et al., 2002). This indicates that UV irradiation could significantly increase the susceptibility of high DS CA to biodegradation.

4. The effect of material modifications on the degradation process

A faster degradation rate could decrease the impact of CA products, such as cigarette butts, on the environment (Quintana et al., 2013). Considering the demands for more sustainable and environment friendly products, several strategies have the potential to increase the degradation rate of CA in natural environment as depicted in Fig. 3. The concept is, however, challenging as the modifications also commonly alter the properties of the material. Furthermore, this approach could increase the risk of littering if the consumer considers the product to be degradable in natural environments.

4.1. Chemical functionalization

The abundant hydroxyl groups along cellulose and cellulose acetate backbone provide handles for further modification. This has opened new research field utilizing these functional groups for large range of chemical reactions (Malmström and Carlmark, 2012; Carlmark et al., 2012). As an example, polyesters have been grafted onto CA chain via ring-opening polymerization (ROP) (Teramoto et al., 2002; Vlček et al., 2008; Vidéki et al., 2005; Lemmouchi et al., 2014). Recently cellulose acetate was also modified by covalent attachment of oxidized carbonized products and also reinforced with nanofibrillated cellulose, which could potentially enhance both hydrolytic and photo-oxidative degradation of CA materials (Gustavsson et al., 2020; Wang et al., 2017). All above modifications are expected to influence the susceptibility of cellulose acetate towards different environmental factors. For example, grafting with readily biodegradable aliphatic polyesters could potentially enhance the degradation rate compared to merely acetylated materials (CA). There is high need of more systematic experimental work with proper characterization of the changes taking place and the extent of degradation to increase the knowledge of structure-degradability relationships.

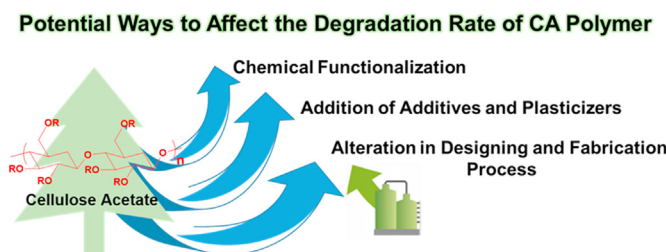


Fig. 3. Potential ways to affect the degradation rate of CA polymer.

4.2. Additives that enhance photodegradation

One way to try to promote the “environmental degradation” of plastic materials is the addition of photosensitizers into the plastic materials (Hosono et al., 2007a). This approach has been most widely explored for enhancing the environmental degradation of polyethylene. In the case of polyethylene this has not been successful as the degradation slows down after the initial oxidation and/or fragmentation (Roy et al., 2011). However, this approach could be more successful if the formed fragments would have inherent degradability. Endo et al. investigated the effect of photosensitizers and photoacid generators on the photodegradation of CA polymer (Hosono et al., 2006, 2007a, 2008). The studied compounds included benzophenone, acetophenone, 4,4'-bis(dimethylamino)benzophenone and its derivatives such as o,c-diethoxyacetophenone, quinones, thioxanthenes and phthalocyanine. The observed molar mass decrease, increased molar-mass dispersity and formation of CO₂, CO, and acetic acid indicated cleavage of the glucosidic bonds (Hosono et al., 2007b). Incorporation of photoacid generators, such as triphenylsulphonium trifluoromethanesulfonate (TPS), and diphenyliodonium trifluoromethanesulfonate (DPI) into the CA films, which were subjected to UV light ($\lambda = 275$ nm), resulted in release of acetic acid as well as sulfonic acid as by-product (Hosono et al., 2007b). The acetic acid release was further accelerated by addition of benzophenone, as a triplet state sensitizer for DPI (Hosono et al., 2008).

The incorporation of TiO₂ type photocatalysts has also been investigated to accelerate the degradation of CA (Egerton and Shah, 1968). The addition of high surface area TiO₂ additives (≥ 50 m²/g) into CA fibers provided enhanced photodegradation rates (Itoh et al., 1998). To further enhance the photoactivity of TiO₂, surface treatment of TiO₂ with barium phosphate (Irick, 1993) and utilization of nano-structured ultrafine anatase pigments with large specific surface area, have also been evaluated (Jang et al., 2007; Brodof and Hopkins, 1996). Finely dispersed non-transition-metal-modified TiO₂ particles were also evaluated for fabrication of catalytically degradable CA materials (Hölter and Koppe, 2016). The incorporation of photocatalytic TiO₂ resulted in moderate increase in the photodegradation rate of the CA films, which was attributed to increased hydrophilicity, surface area and lowered zeta potential due to the photocleavage and photooxidation. With no UV irradiation the CA films with different TiO₂ contents were not susceptible to enzymatic degradation by a cellulase from *Aspergillus niger*. After UV irradiation, the biodegradation rate of all the films with and without TiO₂ increased significantly (Jang et al., 2007).

4.3. Addition of plasticizers, water-soluble adhesives or polymers

Plasticizers are used to produce flexible plastic products for different applications. The addition of plasticizers also influences the degradability of the material. Hydrophilic plasticizers or blend components generally increase the susceptibility towards e.g. hydrolysis as the material is able to take up more water (Andersson et al., 2010; Quintana et al., 2016; Boulven et al., 2019). However, the risk with this approach is that dissolution of the water-soluble component is counted as enhanced degradability. There are stringent requirements on the use of plasticizers since they are generally added in large quantities and are commonly prone to migration and release into the environment during product use. The softening temperature of cellulose esters is close to decomposition temperature, this results in need of plasticizers for successful melt processing (Yoshioka and Shiraishi, 2000). Diethyl phthalate, dimethyl phthalate, and triphenyl phosphate have been commonly used as plasticizers for cellulose esters. Other plasticizer candidates and additives have also been evaluated including citric acid esters such

as acetyl triethyl citrate (Ghiya et al., 1996). Simple triglycerides such as triacetin have been used in cigarette filters to accelerate the degradation rates (Lee and Shiraishi, 2001). The high boiling point of triacetin could decrease the loss of plasticizer during melt processing. Hydrophilic low molar mass polyethylene glycol blended with CA decreased the T_g of CA and was reported to enhance the degradation rate under accelerated weathering conditions (Quintana et al., 2013; Rosa et al., 2005). CA and its degradation products are assumed to be safe for the environment, but migration of some common CA plasticizers, especially phthalates, could cause negative influence on our health and environment (Zepnil et al., 2012; Ghebremeskel et al., 2007). Haynes et al. showed the visible difference in appearance of two samples in the presence or absence of plasticizer (Haynes et al., 1991). The migration and evaporation of plasticizers and their reactions with other chemicals in the surroundings has also been reported (Schilling et al., 2010). As a result, potentially unsafe plasticizers and plasticizer degradation products could be released to surroundings, leading at the same time to deterioration of material properties and appearance.

Aiming to accelerate the degradation rate of CA, water-soluble polyesters have been blended into CA fibres. The idea was that the additive would dissolve during water exposure, which would disintegrate the individual fibres (Morie and Sloan, 1977, 1978; Tsugaya et al., 1999). Water sensitive hot melt adhesives were utilized in plug wraps to enhance the biodegradability potential in contact with aqueous environments. Other water-soluble adhesives, such as acrylic polymers, polyalkylene oxide and polyethers have also been evaluated (Yamashita and Endo, 2004). Biodegradability of blends of CA (DS 2.5) with starch (St, 25 wt%) and propylene glycol (PG, 19 wt%) were investigated under composting, soil and marine conditions. Soil burial and composting experiments of CA/St/PG blends revealed preferential degradation of propylene glycol and starch (Mayer et al., 1995; Bastioli et al., 2004). Another study demonstrated complete biodegradation of CA after 200 days of controlled composting, while CA plasticized with 30% triacetin or triacetin-diacetin was completely biodegraded after only 46 days (Phuong et al., 2014). With only 20 wt% of plasticizer this effect was not achieved. More research is needed to understand the potential accelerating effect of different modifications. From practical point of view the addition of e.g. water-soluble components could restrict the use of the material in many conventional polymer applications due to the sensitivity against water.

4.4. Alterations in design and fabrication processes

It is of high interest to understand how the design and fabrication of CA products including networks of cellulose acetate fibres, membranes and filters affects the disintegration process under natural and accelerated conditions. Reducing the entanglements and introduction of physical imperfections are possible approaches to accelerate the disintegration process (Lipowicz et al., 2011). As an example, slits were introduced to filters aiming at enhanced biodegradability (Wilson and Harris, 1999). It was proposed that CA filter elements that have a core consisting of biodegradable fibrous or particulate cellulose coated with cellulose esters (Sebastian et al., 2012) or stapled short fibers instead of continuous fibers (Berger and Sproull, 1972) could enhance the ultimate degradation of the filters. It has also been proposed that filters prepared from unwoven fabric sheet could more readily disintegrate leading to enhanced susceptibility to biodegradation when discarded in natural environments (Yamashita, 2004).

5. The case of cigarette butts

Cigarette butts (CBs), made of cellulose acetate are the most

common littered items potentially polluting the environment with microplastics (National Geographic, 2019; Novotny et al., 2009). The tobacco industry's international research organization (COR-ESTA), formed a "Cigarette Butt Degradability Task Force" in the early 1990s to establish the degradability of CBs. According to Philip Morris International: "Even if we create a biodegradable filter, it will be extremely important not to send the wrong message that it's okay to litter" (Hicks, 2019). This is a general concern for all biodegradable plastics, i.e. the possible effect of increased littering when people get the perception that the material will disappear if left in the nature.

Some solutions have been suggested in the literature to recover and recycle CA materials used in cigarette butts (CB) (Benavente et al., 2019; Zhang et al., 2020). Development of collection and recycling processes would reduce the release of harmful materials into the ecosystems and support the circular economy and sustainable development. Potential options for the end-of-life management of CA products, especially CBs, have been explored in several studies. Woodring proposed that serious legislation is required in the form of a butt tax to fund clean-up efforts and/or to give rebates for smoked cigarettes at public collection points (Ocean Recovery alliance, 2019). Terracycle in New Jersey recycles CBs to park benches and shipping pallets. The recycling process is however not economically fully viable and it is partly funded by tobacco companies. CBs have also been evaluated as raw materials for supercapacitors for energy storage (Xiong et al., 2018; Lee et al., 2014). Porous carbons derived from CBs exhibited super porous, ultra-high surface area and pore volume had good hydrogen storing capacity and could also adsorb water contaminants (Blankenship and Mokaya, 2017; Li et al., 2020). The use of CBs as precursors for the development of carbon quantum dots with strong fluorescence was also demonstrated (Anmei et al., 2018). The economic sustainability of the processes, the consumption of energy and/or reagents, as well as the toxicity of the outputs have not been extensively studied (Marinello et al., 2019).

The previous studies show that deacetylation process and subsequent further degradation of CA can be accelerated by additives or favourable degradation conditions. However, full degradation of CA based materials or CBs under "normal natural conditions" has not been shown. According to a recent study, the weight loss of CBs ranged between 20 and 30% after 2 years of aging under laboratory and field conditions (Bonanomi et al., 2015; Bonanomi et al., 2020), which is far from complete degradation to CO₂, or biomass. Aside from their environmental persistence, CB waste can also pose a threat to biological organisms living in terrestrial and aquatic ecosystems mainly due to the content of nicotine, heavy metals and other chemicals (National Geographic, 2019; Wright et al., 2015; Slaughter et al., 2011; Suárez-Rodríguez et al., 2013). Recently, CBs were classified as hazardous according to the European regulations based on the ecological toxicity tests (Rebischung et al., 2018). These negative effects were derived to the nicotine and other contaminants in the CBs.

6. Summary and future outlook

Depending on the plastic material and its application plastic products should be designed for mechanical or chemical recycling or composting (biological recycling). Degradability of plastic material is always connected to specific environment, general "environmental degradability" cannot be guaranteed and ensuring rapid and complete degradation of plastics in the wide range of natural environments would be very difficult. Throwing plastics in the nature should not be considered as a proper or acceptable end-of-life management option. However, some products have high probability of ending up in the nature and enhanced degradability

in common natural environments could be a benefit.

In this review, we have highlighted the complicated process of "environmental degradation" with cellulose acetate as a model polymer. Biopolymers are inherently degradable in common natural environments although the time-frame differs greatly depending on the actual condition. The influence of chemical modifications needed for use of biopolymers in plastic applications on the inherent degradability is still poorly understood. Most chemical modification inhibit the degradation process, but there are also strategies to accelerate the degradation rate by chemical modification or different additives. In the case of CA, for example, high degree of acetylation is crucial for good thermoplastic properties. At the same time high degree of acetylation lowers the degradation potential. As deacetylation is crucial for further biodegradation of high DS cellulose acetate, this highly further limits the number of favourable degradation environments and conditions. We still need to learn how to overcome these barriers in order to successfully design materials for optimized service-life performance and different end-of-life options. This requires in-depth understanding of the complicated interplay between structure, environment and degradation process. There is need for more systematic studies with thorough molecular level characterization of original structures and changes taking place under different environmental conditions to understand structure-environment-degradation relationships. Simple growth of microorganism on the surface of the materials or weight loss that could be due to loss of additives or degradation of low molar mass fraction in the materials should not be considered as proof of degradation. Partial weight loss should also not be considered as a proof of final complete degradability of the material.

CRedit authorship contribution statement

Nisha Yadav: Writing - review & editing. **Minna Hakkarainen:** Conceptualization, Writing - review & editing.

Declaration of competing interest

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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