Paper Drinking Straws Coated with Cellulose Acetate and Polyhydroxyalkanoates *via* an Entropy-Driven Approach and Natural Colorants as Alternatives for Plastic Drinking Straws

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As a way to reduce microplastics or nano-plastics in the ocean, it is of interest to develop biodegradable paper-based drinking straws to replace non-degradable plastic drinking straws. Primary questions to be addressed include how to design suitable coatings for paper drinking straws. Such coatings not only need to resist water. In addition, consumers have high expectations for the strength of a drinking straw. It is proposed here to replace non-biodegradable polypropylene, which is presently the main component of straws, with biodegradable and hydrophobic coating components *via* an entropy-driven approach. It is further proposed to develop colored paper-based drinking straws with cellulose nematic liquid crystal photonic pigments as a way to make the product stand out visibly, while at the same time mediating the usage of toxic chemical pigments.

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Paper Drinking Straws as Alternatives of Plastic Drinking Straws

Plastic drinking straws have become routinely used items in daily life, and most of them are made of polypropylene (PP). The United States uses about 6.3 to 14.2×10^{10} plastic drinking straws annually (James *et al.* 2024). However, these single-use PP plastic drinking straws cannot be biodegraded in the marine environment and cause ocean plastic pollution issues, such as micro-plastics and nano-plastics. Development of biodegradable cellulose paper drinking straws has attracted significant attention, such as by Coca-Cola and Starbucks Coffee companies. Such efforts are prompted by the merits of cellulose-based paper, such as an abundant resource, low price, and biodegradability. Paper has inherent drawbacks from the perspective of making drinking straws, such as low water resistance and weak mechanical properties (Gutierrez *et al.* 2019). Inspiration comes from water-barrier paper cups, which are laminates of paper with polyethylene or poly(lactic acid) [PLA]. These are formed *via* a hot-press and extrusion lamination or a spray and extrusion coating. In principle, such a system has potential as a way to make drinking straws.

A Concept of Water Barrier Paper-based Drinking Straws

As a biodegradable, recyclable and hydrophobic biopolymer, polyhydroxyalkanoate (PHA) is produced *via* a biological fermentation process of sugars or lipids (Joyce *et al.* 2018). The PHA family involves poly(hydroxybutyrate-co-valerate)

[PHBV], poly(hydroxybutyrate) [PHB], and poly (3-hydroxyvalerate). As one of the most promising biopolymers, the PHB, first discovered by Lemoigne in the 1920s (Lenz and Marchessault 2005), has similar thermal and mechanical properties to isotactic PP. The lamellar structure of PHB contributes to its excellent gas and water barrier properties, making it suitable for paper drinking straw materials. Therefore, PHB is an ideal coating material to tailor the water resistance performance of paper. However, PHB as a paper coating is still far from widespread usage, which is due to some inherent restrictions. One restriction is that the hydrophobic PHB cannot form a uniform coating on the hydrophilic paper substrates. Another restriction to its application is its relatively high price and limited availability compared to conventional synthetic polymers. Therefore, there is a high incentive to find another synergistic component to achieve its excellent interfacial adhesive with paper substrates and meanwhile reduce its loadings as a coating component by partially replacing it with a relatively low-price readily available and biodegradable material.

However, miscibility is a follow-up question to find synergistic materials in paper coatings. According to the thermodynamic analysis perspectives, enthalpy makes a major contribution in promoting polymer miscibility compared to entropy (Rubinstein and Colby 2003). Interestingly, a recent study has put forth a rule in terms of entropy-driven miscibility (Hou *et al.* 2023). For instance, the relatively low Flory-Huggins χ parameter contributes to miscibility in the PHB-Polyvinyl Acetate (PVAc) or PHBV-PVAc blends (Hou *et al.* 2023). However, PVAc is not an ideal synergistic component, as it is not fully biodegradable. Cellulose acetate (CA) as a cellulose derivate has a similar chemical structure to PVAc, so CA and PHB or PHVB should have a good miscibility according to the rule proposed by Hou *et al*., which is also supported from synchrotron small angle X-ray scattering and differential scanning calorimetry data (El-Shafee *et al.,* 2001). Therefore, cellulose acetate as a synergistic component of PHB blends for paper coatings is an environmentally friendly strategy, potentially providing material for producing paper drinking straws with superior water barrier and biodegradable properties. Another merit of CA is its inherently amphiphilic character. It not only has a good miscibility with cellulose paper substrates but also enhances water-barrier properties of cellulose papers, which can be attributed to the penetrated and locked CA in paper pores (Kwak *et al.* 2022). Therefore, PHB and CA blend coatings are expected to contribute to enhanced water-barrier properties of papers. Research is needed to determine what ratios of PHB to CA are required to achieve excellent overall-performance of paper coating materials. Fortunately, the high CA loadings could compensate for the relatively high price of PHB. However, a relatively high degree of substitution (DS) of the CA is not readily biodegradable, as the acetyl groups attached to the cellulose backbones hinder the degradation enzymes from reaching the celluloses (Tyagi *et al.* 2022). Therefore, an optimized CA product could serve as a synergistic component in PHB blends to produce coating papers for fully biodegradable paper drinking straws.

Color-Paper Drinking Straws from Cellulose Liquid Crystal Pigments and Natural Colorants

Conventional paper drinking straws have excellent biodegradability compared to plastic PP drinking straws. However, to achieve the vivid structural colors of paper straws is a tough goal. Conventional chemical pigments and dyes have inherent environmental issues and cannot be degraded in the ocean. Fortunately, self-assembled ethylene cellulose, hydroxypropyl cellulose, and cellulose nanocrystals form chiral nematic liquid crystal structures, and these cellulose liquid crystal photonic pigments display a broad range of structural colors, which are ideal alternatives of toxic chemical pigments. These cellulose liquid crystal photonic pigments can maintain their structural colors after fragmentation (Droguet *et al*. 2022). Further, natural colorants have emerged as an environmentally benign material due to their non-toxicity and biodegradability if they can be economically sourced.

Summary

Globally, considerable efforts are underway to combat the environmental pollution caused by single-use plastics, including plastic straws. Paper straws, which dominated the market until the early 1960s, gradually faded away as plastic straws, known for their durability, became the preferred choice for consumers seeking a sturdier option for their drinks. To reverse this trend and shift back to paper straws, using a masterbatch of PHB, CA, and cellulose liquid crystal or natural pigments *via* solution coating or melt extrusion could be a promising approach to producing coated color papers as drinking straws that not only offer a durable option to consumers but also benefit the planet.

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