Barrier Molded Fiber Products Based on Recovery and Up-cycling of Paper and Agricultural Wastes *via* a Pickering Emulsion Approach

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To reduce plastic pollution, it is of interest to develop biodegradable molded fiber products from recovered cellulose-containing residues as an alternative to single-use plastics. Primary questions to be addressed include how to compound molded fiber products from the recycling of paper or cardboard and agricultural residual wastes *via* combined vacuum thermo-forming and post-drying or synergistic cold and hot press approaches. In addition, consumers will have high expectations regarding barriers for moisture and grease. It is proposed here to produce uniform barrier molded fiber products *via* a Pickering emulsion approach with chemically recycled waxes from thermolysis of waste polyolefins. It is further proposed to develop a closed-loop process for recyclable molded products and up-cycling lignocellulosic fibers reinforced biomass-derivable vitrimer bio-composites for sustainable packaging. The development of molded fiber products makes it possible to mitigate the usage of single-use plastics.

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Molded Fiber Products as an Alternative to Single-Use Plastics

Single-use plastics, primarily from petroleum-based polymeric materials, are the most used material for packaging containers, shopping bags or pouches, and table-wares. However, disposal of single-use plastics at the end of their service life causes serious environmental pollution. This has prompted tremendous effects toward developing alternative sustainable materials. Molded fiber products composed of natural fibers (*e.g.*, wood pulps and bamboo fibers) are highly regarded in terms of biodegradability, recycling, light weight, and food compatibility. They are considered as promising alternatives to single-used plastic products. The primary compounding approaches involve thermoforming or combined cold and hot pressing. The typical protocols of molded fiber products are composed of two main processes, namely, pulp preparation and a molding process involving vacuum forming or cold pressing, and then a drying process.

Large amounts of paper waste and agricultural residues generated each year are not appropriately managed. With environmental concerns rising, there is more incitive to recycle agricultural residues, and paper and cardboard wastes. The content of cellulose or lignocellulosic fibers in these recovered materials are good sources for molding fiber products (Lo *et al.* 2024), *e.g.*, disposals of single-used paper cups from Coca Cola in Atlanta and Starbuck in Seattle, shopping paper bags or pouches from Jet Paper Bags in New Jersey, and wood fiber wastes in primary States of Maine, North Carolina, and Oregon, and sugarcane bagasse residues in main States of Louisiana, Florida, and Hawaii.

The resulting molded fiber products currently perform the roles of cutlery, cups, and packaging containers and promising as fiber bottles and caps as alternatives of expanded polystyrene containers, polyethylene terephthalate plastic bottles and polypropylene bottle caps.

Molded Fiber Products with Enhanced Barriers, Close-Loop Chemical Recycling, Up-cycling, and Biodegradability *via* Pickering Emulsions

Resistance to water and grease are crucial for many applications of molded fiber products. Due to the intrinsic hydrophilic character of lignocellulosic fibers, there is a need for eco-friendly barrier layers. Waxes as coating materials are common approaches to enhance barrier properties of packaging materials in industry. However, the large production and utilization of petroleum-based waxes inevitably causes toxic gases emissions, thereby enhancing barrier properties at the cost of sustainability. Alternatively, the development of natural waxes has attracted attention such as barrier coatings, *e.g.*, soybean oil and beeswax. However, the plant- and animal- bio-waxes have intrinsic limitations in terms of types and sources for the barrier coating industry. Recently, the up-cycling of waste polyethylene (PE, *e.g.*, high-density and low-density PE) and their mixtures of polypropylene to produce waxes and fatty acids in high yields and purities as chemically recycled waxes have been reported *via* a gradient-temperature thermolysis method (Xu *et al.* 2023). A follow-up method to chemically recycle waxes from PE and metallic PE was optimized in terms of yield and purity with table salts. However, enhancing barriers of molded fiber products with up-cycling waxes is challenging owing to their hydrophobic nature with low solubility in aqueous solution and poor compatibility with molded fiber product surface. Although waterborne polyurethane, polylactic acid (PLA), or polybutylene succinate (PBS) as coatings are an alternative approach, there are intrinsic restrictions. The use of an oil-in-water Pickering emulsion as a carrier of waxes is an interesting perspective to produce uniform hydrophobic coatings. By stabilizing the waxy droplets with a coating of nanocellulose (CNC), hemicellulose, or its derived xylan nanocrystal (XNC) (Meng *et al.* 2021; Hao *et al.* 2022), it is possible to produce uniform coatings and subsequently impart fiber surfaces with hydrophobicity. However, CNC, hemicellulose, or XNC stabilizers need to be tailored to optimize their amphiphilicity to produce Pickering emulsion with a long-term stability. The straightforward methods are grafting aldehyde groups on CNC or the hemicellulose and XNC backbone from periodate oxidation or its reducing end with diverse amine compounds with different structures and varied carbon lengths of alkyl groups *via* a Schiff base reaction, *e.g.*, methylamine, ethylamine, isopropyl amine, and benzylamine (Solomons and Fryhle 2011). Alternative approaches are polyelectrolyte interactions such as coacervation or electrostatic interactions with negatively charged CNC, hemicellulose, or XNC and oppositely charged synthetic polyelectrolytes *via* controlled radical polymerization, *e.g.*, reversible addition-fragmentation chain-transfer and atom transfer radical polymerization (Odian 2007). In addition to water and grease barriers, the rod- or platelet- like CNC, hemicellulose and XNC nanoparticles also contributes to gas barrier performance, *e.g.*, oxygen and carbon dioxide barriers. To further enhance grease barriers, biodegradable poly(lactic acid) PLA or poly(butylene succinate) PBS, as synergistic agents for up-cycling of waxes dissolved in the oil phase, make it possible to enhance molded fiber products with both enhanced water and grease barrier performance in addition to gas barriers. Other fillers such as nano-clay and nanotube stabilizers can also be considered for Pickering emulsion coatings. The follow-up question is about the close-loop recycling and up-recycling of molded fiber products. Similarly to the chemical recycling of barrier papers, molded fiber products can be cut into small pieces and then resuspended as fibers with the use of sodium hydroxide at low concentrations. The re-pulped and remolded products are expected to maintain mechanical performance under ideal scenarios to achieve the ideal close-loop chemical recycling with multiple cycles. Alternatively, the re-pulped fibers make it possible to be compounded into fiber sheets, then infused with biodegradable PLA- or PBS- based vitrimer materials, and subsequently compounded *via* hot-press lamination for the preparation of high-performance lignocellulosic fibers reinforced biomass-derived vitrimer bio-composites. Such products can be applied in biodegradable cutlery, composite packaging, and shape memory and self-healing functional composites (Clarke *et al.* 2024). Thanks to the reversibly dynamic covalent structures of vitrimer materials, the composite materials also make it possible to achieve chemical recycling multiple times (Wu *et al.* 2024).

Another question is the biodegradable performance of molded fiber products and up-cycling lignocellulosic fibers reinforced composites, especially degradation in ocean environments. Soil burials and marine-water field trials are primarily methods for their biodegradable performance evaluation. The variation in terms of molecular weight and crystallization can be tracked to *in-situ* evaluate biodegradable performance, *e.g.*, size exclusion chromatography and differential scanning calorimetry. Therefore, barrier molded fiber products have potential for diverse applications in packaging industries, and its market potential in USA for next 10 years is promising. The next step is committed to promote the barrier molded fiber products toward the real USA market from the lab-scale mode by start-up companies with the endorsements from USA venture capital fundings, *e.g.*, seed fundings. Overall, the prospective and lucrative barrier molded fiber product market are promising in the next 10 years despite its current status in its infancy of product development.

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