

Grinding and Extrusion Treatments: New Trends in Green Extraction

Lorenzo Gallina, Emanuela Calcio Gaudino, Giorgio Grillo, Silvia Tabasso, Giancarlo Cravotto Department of Drug Science and Technology, University of Turin, Via P. Giuria 9, 10125 Turin, Italy

Mechanochemistry and extrusion

Mechanochemical treatments are the oldest humankind's processes. By grinding with a mortar and a pestle, the first extractions of natural pigments from biomasses were performed in prehistorical time. Today, after thousands of years, mechanochemical processes are exploited again as frontiers in extraction and synthesis due to their advantages in terms of economic and environmental sustainability. The use of reactive extrusion in extraction and biomass conversion is just at the beginning, and more studies are needed to discover its true potential.





Polyphenols-blended polymers

Blended and functionalized polymers can act as a protective package for food products, avoiding oxidative degradation. Extracts rich in polyphenols can be used to prepare such blends. A PEAA*-polyphenols extract blend was prepared, using subcritical water extracts of chestnut peels. β -cyclodextrins were added to preserve polyphenols during the extrusion process. Before and after the extrusion, antioxidant activity was monitored with DPPH[.] assay. The test was performed both directly on the blend and after release by contact with MeOH (20 min). CPPE* mantained a good radical scavenging activity through all conditions tested, and cyclodextrins protected the extract from degradation during the extrusion process.





Main steps of blend preparation: (a) PEAA beads coated with β -CD/CPPE before extrusion b) extrusion of the β -CD/CPPE-PEAA blend, and (c) the obtained blended PEAA: β -CD-PEAA (left) and β -CD/CPPE-PEAA (right) for comparison

Biomass delignification





The production of platform chemicals and bioethanol from biomass is hindered by the presence of lignin, which needs to be removed. Among the various methodologies already developed, little has been done on lignin removal by reactive extrusion. Exploiting reactive extrusion in delignification processes means avoiding solvent usage and consuming less energy. Wheat-straw biomass was subjected to mechanically induced delignification by reactive extrusion under basic conditions. Biomass was extruded with NaOH beads at 190 °C for 1 min at 40 rpm without pretreatment. FESEM images show that the ordered fiber became roundish and lost their spatial orientation. Characterization by NREL showed a lignin content of 1.8% in the extruded biomass, in contrast with the starting 21.8%.

Left: Raw biomass, compact and ordered bundles of small fibers with smooth and fairly intact surfaces **Right:** Biomass after extrusion with NaOH beads. Previously ordered fibers are now disordered and roundish.

Hemp biomass blended polymers

Hemp is used as a textile fiber since antiquity for its excellent mechanical properties. Its production continued until today and reached up to 250 thousand tons in 2020, being promoted by the European Union.

Hemp fiber can be extruded with polymers to create blends: these



blends can then be used for various applications instead of pure polymers, reducing plastic usage. Bio-blends can also be generated using biopolymers, preparing a biodegradable blend. Blends were produced by mixing micronized hemps in different proportions to various polymers, namely PEAA, LDPE and PLA*. Produced blends are now being tested for their mechanical properties, to assess their suitability for industrial purposes.

> *PEAA: Poly(ethylene-co-acrylic acid) LDPE: Low density polyethylene PLA: Polylactic acid



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Green Extraction of Natural Products