Innovative Strategies for Sustainable Materials: Developing Protein-Based Bioplastics from Rapeseed By-Products for a Circular Economy

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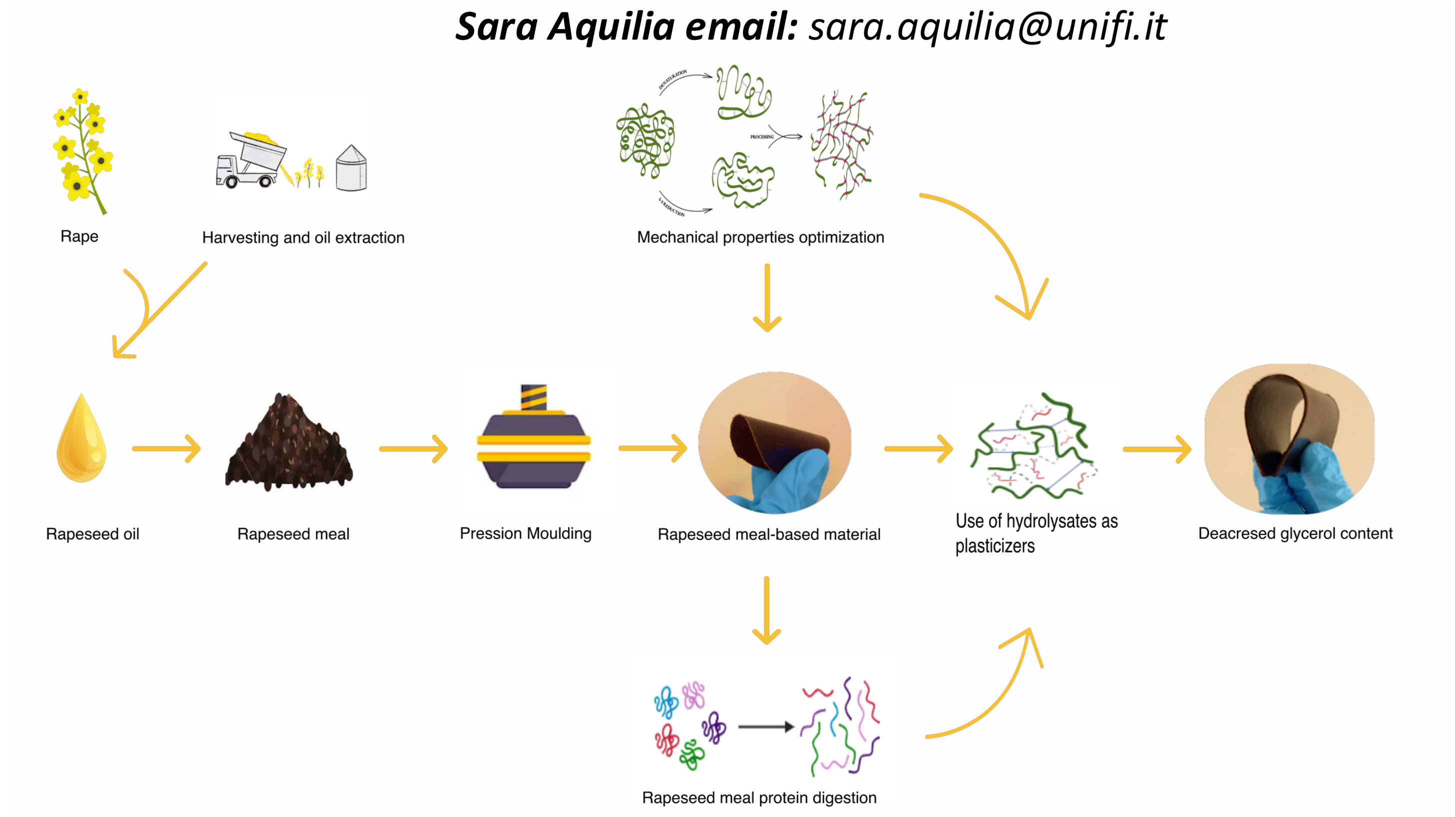
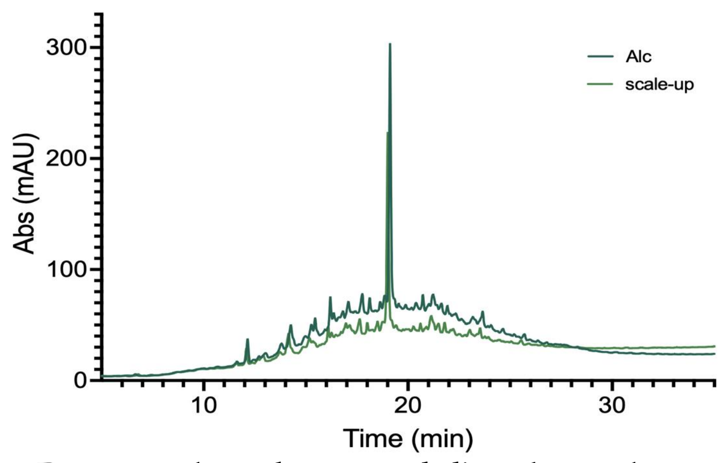
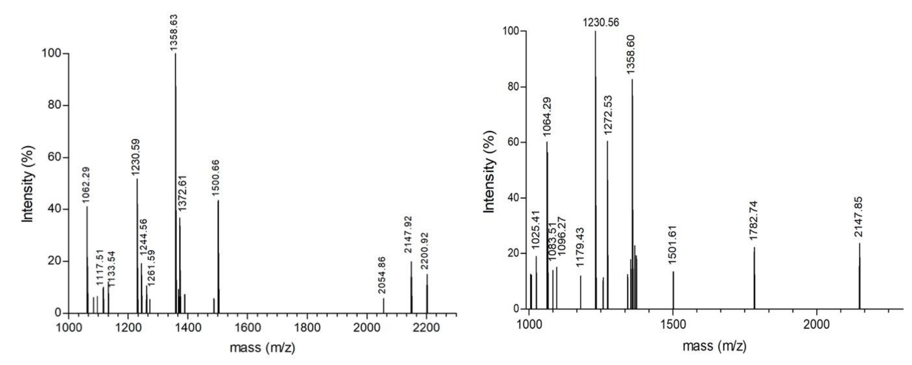
Bioplastics derived from coproducts or waste materials offer the advantage of exploiting pre-existing, underutilized resources.[1] Among these, natural biopolymers, specifically proteins, emerge as an attractive alternative to petroleum-based materials both in terms of potential applications and environmental impact.[2] The presented study is a proof-of-concept of the development of a protein-based cross-linked material with plastic response for multiple applications. Whole rapeseed protein-rich meal has been chosen as main ingredient and pression-moulding process was evaluated as an efficient method to produce a protein-based material.



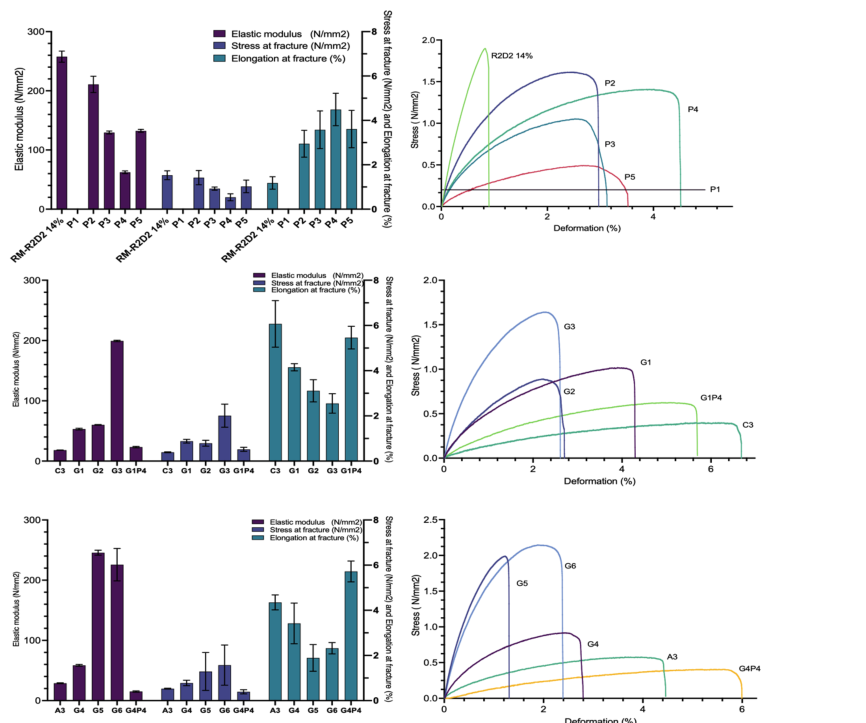
Samples were collected from a by-product of the crude oil production after oil pressing and hexane extraction process.[3] Meal/glycerol/cross-linker/protein-based compatibilizer blends (RM) were mixed with sodium sulfite (Na_2SO_3) and different denaturants (SDS, urea, guanidine) to obtain protein denaturation during thermal processing, thereby enhancing the strength and toughness of the final materials. Furthermore, this research extends its focus to the proteolysis of rapeseed proteins using specific proteases directly on rapeseed meal, generating peptide mixtures. These hydrolysates have been used as components of the protein-rich materials, with the aim of achieving a full eco-sustainability.

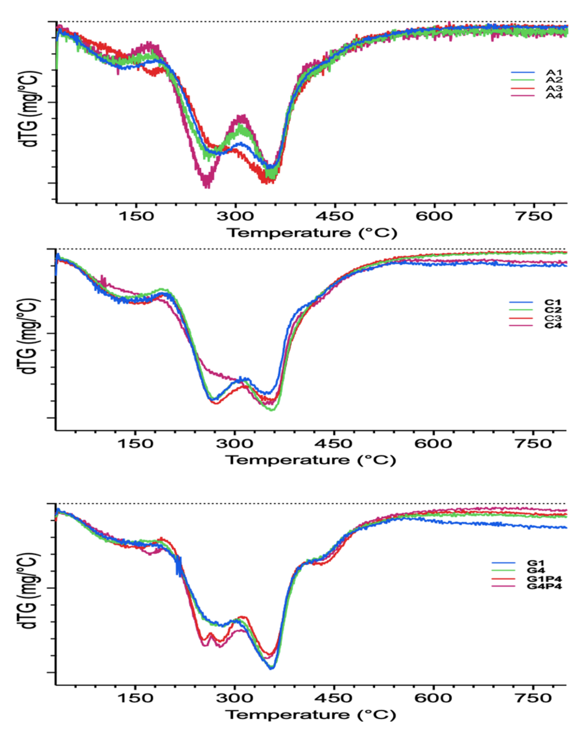
USE OF HYDROLYSATES AS PLASTICIZERS



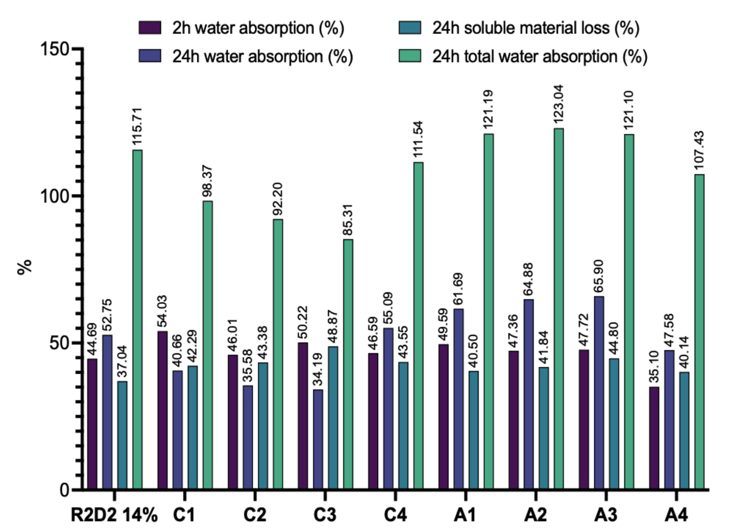


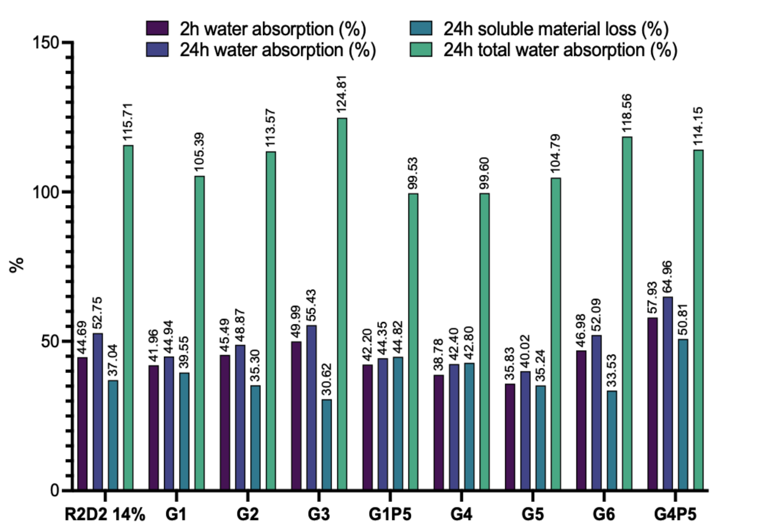
Proteases have been used directly on the raw meal to obtain peptides, which were strategically designed as additives in protein-rich materials. A preliminary screening of the hydrolysates was conducted via RP-HPLC and MALDI-TOF-MS, revealing the formation of hydrophilic peptides with masses ranging between 1000 and 1500 Da. Scale-up of the process was set-up in semi-industrial scale.



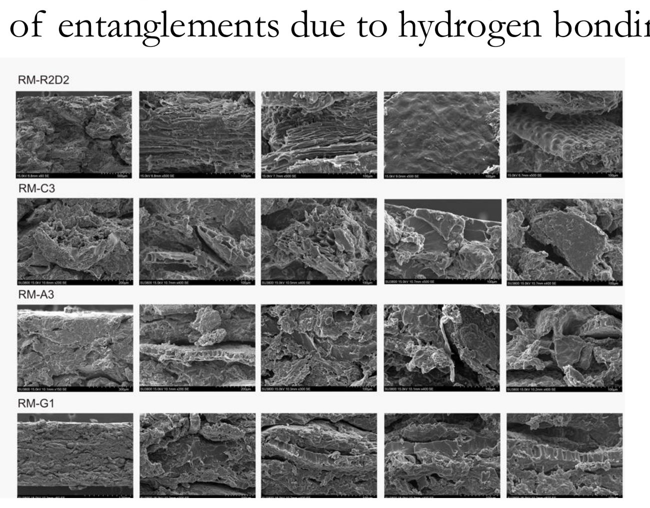


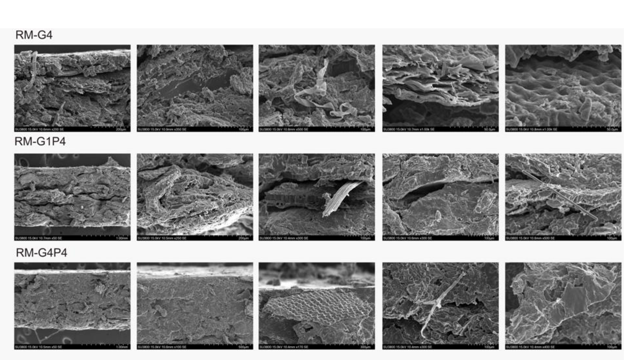
Rapeseed hydrolysates and collagen hydrolysates functioned efficiently as plasticizers due to their hydrophilicity and low molecular weight. Stress-strain analysis indicates a reduction in Young's modulus and a significant increase in elongation at break. Thermogravimetric analysis (TGA) revealed enhanced thermal stability, particularly in materials with a reduced glycerol content in the mixtures.





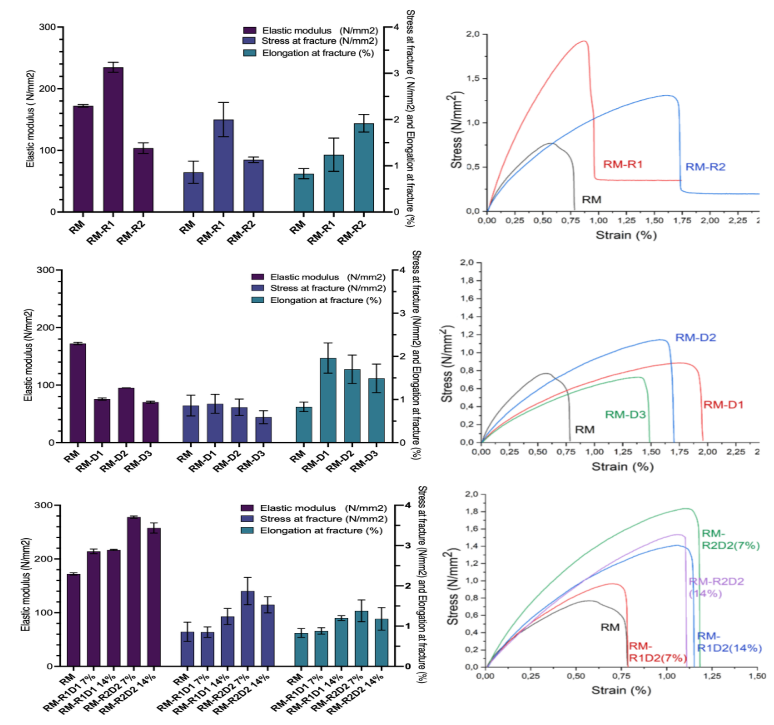
All the specimens exhibited improved water absorption, attributed to the increased formation of entanglements due to hydrogen bonding between the protein matrix and the hydrolysates.

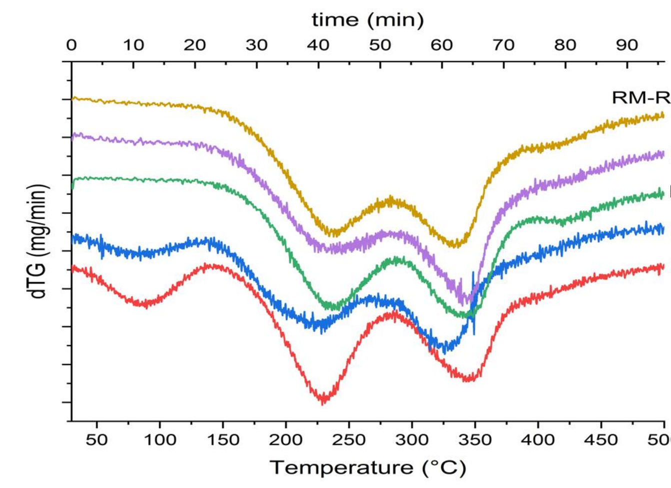




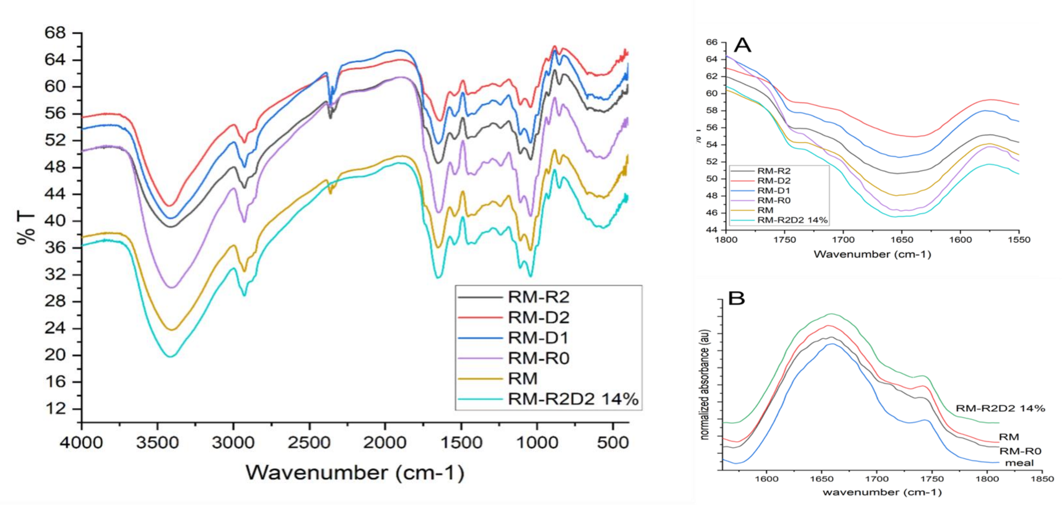
All specimens retain a layered structure, likely due to insufficient applied pressure. However, the G4P4 material exhibits a uniform morphology at 50 and 100 μm. Particles of the raw material are still visible to varying degrees.

USE OF PROTEIN DENATURING AND S-S REDUCING AGENTS



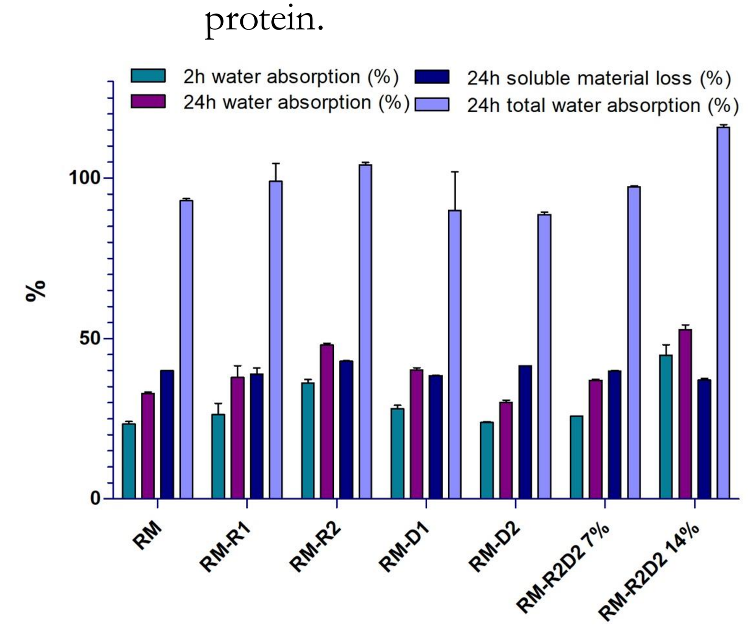


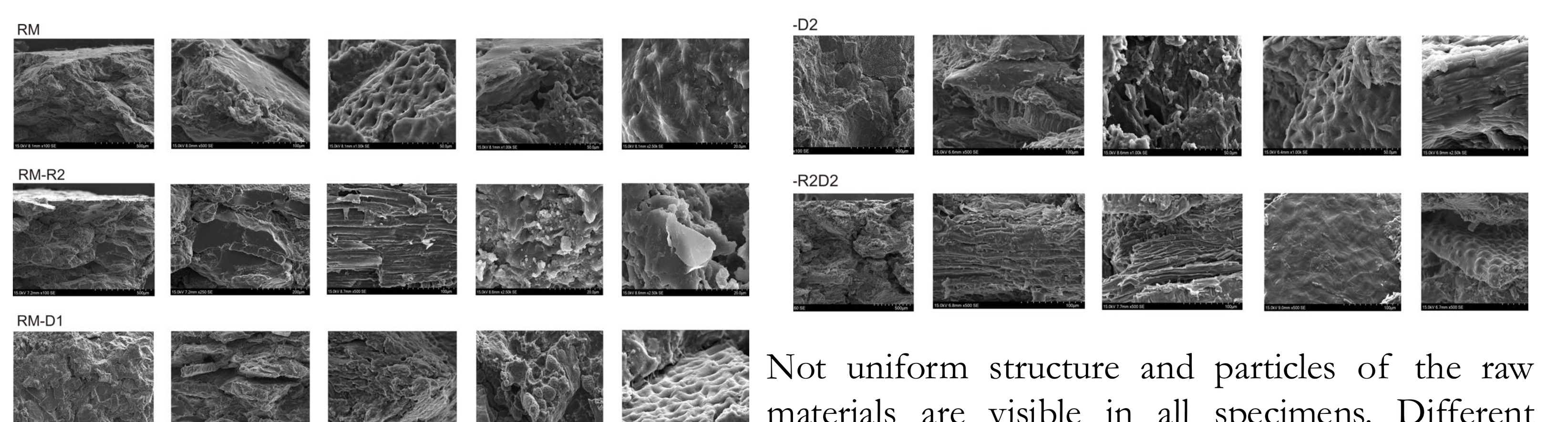
Different S-S reducing and denaturing agents were tested at various concentrations to induce protein denaturation and to understand the role of the molecular feature on the material ultimate properties. The polypeptide chain became so more flexible and, at the same time, made functional groups more accessible for crosslinking reactions. Moreover, Thermogravimetric analysis (TGA) revealed improved thermal stability of the material containing both the reducing and the denaturing agent (RM-R2D2 14%).



A change in protein structure was evidenced by the FT-IR analysis when comparing the amide I bands of the specimens with different composition to each other and to the one of rapeseed meal, indicating effective protein denaturation. The presence of the reduced disulfide bond and of the denaturing agents causes partial unfolding of the proteins and led to a major exposure of the amino acid side chains in the protein.

In all specimens, there was an approximate 40% loss of soluble material, with glycerol being the likely primary contributor to this material loss due to migration issues. Additionally, the water absorption remained above 100%





Not uniform structure and particles of the raw materials are visible in all specimens. Different morphologies can be observed in the case of RM-D1 and RM-D2, probably because of the different effect of the denaturing agent used. Among all the specimens analyzed RM-R2D2 is the one that looks as the most compact and uniform material.

CONCUSIONS

Rapeseed meal has a high potential for the use in the production of sustainable materials for multiple applications. Different reducing and denaturing agents were tested to induce protein denaturation. The polypeptide chain became so more flexible and, at the same time, led functional groups more accessible for crosslinking reactions. Enzymatic digestion process on the raw meal has been scaled-up and plasticizers effect of hydrolysates mixtures has been also studied. The study is certainly innovative and informative but the mechanical properties are not yet industrially competitive. However, our study suggests a promising pathway to develop a protein-rich material for industrial applications.[4]

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