



**Transilvania
University
of Brasov**

HABILITATION THESIS

Functional polymeric materials obtained with ionic liquids auxiliaries and additives

Domain: Materials Engineering

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List of abbreviations

AFM	Atomic force microscopy
AI	Allomorph index
AMIM	1-allyl-3-methylimidazolium
ATR	Attenuated total reflectance
BMIM	1-butyl-3-methylimidazolium
Cel	Cellulose
CrI	Crystallinity index
DMIM	1-dodecyl-3-methylimidazolium
DSC	Differential scanning calorimetry
EB	Electron beam
EMIM	1-ethyl-3-methylimidazolium
FTIR	Fourier-transform infrared spectroscopy
G'	Storage modulus (rheology)
G''	Loss modulus (rheology)
G _p	Plateau modulus (rheology)
HDPE	High-density polyethylene
HMIM	1-hexyl-3-methylimidazolium
IL	Ionic liquid
Im	bis (trifluoromethylsulfonyl)imide
LDPE	Low-density polyethylene
LOI	Lateral order index
MI	Moisture index
MTO	methyltrioctylammonium
MWCNTs	Multi-walled carbon nanotubes
NFs	Nanofibers
NIR	Near-infrared
NIR	Near infrared
P	Bis (2,4,4-trimethylpentyl) phosphinate
PET	Poly (ethylene terephthalate)
PLA	Poly (lactic acid)
PMC	Polymer matrix composite
PO	Polyolefin
PP	Polypropylene
PVA	Poly (vinyl alcohol)
RTIL	Room temperature ionic liquid
SEM	Scanning electron microscope
TTDP	Trihexyltetradecylphosphonium
UV	Ultraviolet
VIS	Visible
WPC	Wood polymer composite
WPG	Wood percent gain
XRD	X-ray diffraction

(A1) Abstract

The habilitation thesis *Functional polymeric materials obtained with ionic liquids auxiliaries and additives* presents my research results after obtaining of the Ph.D. in materials engineering in 2010, related to obtaining, processing, and additivating different synthetic and natural polymer materials with ionic liquids. Ionic liquids are a class of organic compounds with negligible vapor pressure, trending in many fields such as materials engineering, energy materials, electrochemistry, synthesis, and so forth.

Throughout the material presented in the habilitation thesis, I have demonstrated the usefulness of different types of *ionic liquids* as antistatic agents, ionizing and UV radiation stabilizers, cleaning agents, solvents, carriers for various polymers. The results also extend to obtaining polymer matrix composites, materials with hydrogen storage capacity, or polymeric gels with increased adsorption capacity towards heavy metal ions or dyes. What makes these ionic liquids unique is their highly tunable character. They can be obtained through synthesis to match practically any desired property value in terms of polarity, thermal and radiation stability, electrochemical window, hydrophilicity/hydrophobicity.

My multidisciplinary scientific achievements (B2 section) are structured into four chapters: 1. *Ionic liquids for the development of polymeric materials*; 2. *Ionic liquids as additives and auxiliaries for polymeric materials*; 3. *Polymer matrix composite materials via ionic liquids*, and 4. *Polymeric gel materials via with ionic liquids*. The thesis also presents discussions regarding the *Evolution and development plans for career development* (B3 section).

Chapter one presents an overview of the main types of ionic liquids, their importance to polymeric materials science, their advantages, and limitations they possess. This chapter also reviews these compounds' primary uses in obtaining and processing synthetic and natural polymer materials.

Chapter two presents my original research results indicating that ionic liquids could tune the properties of polymeric materials to a great extent. This chapter demonstrates ionic liquids' usefulness as UV and ionizing radiation stabilizers for cellulosic materials (cellulose fibers and wood). The polymeric materials present a high uptake affinity for ionic liquids. Their radiation-protecting effect is directly proportional to their ability to be retained on the material's surface (which depends on their hydrophobic character and molecular mass). Ionizing radiation (such as high-energy electron beams) can generate active radical species in ionic liquids, which is useful because it can promote grafts on the polymeric material's surface. Due to their ionic character, ionic liquids can serve as antistatic agents for polymer materials determining an increase in the material's surface electrical conductivity.

The results of my research have indicated that ionic liquids can also serve as plasticizers for cellulosic materials. As opposed to conventional plasticizers, ionic liquids determine a remarkable increase in the strain at the breaking point of cellulose and wood and an increase in the tensile strength due to the macromolecular rearrangements they can promote in polymers.

An application of the ionic liquids was also exemplified in this chapter, as auxiliaries -solvents for different biopolymers and natural resins -, and carriers -dispersing agents for particulate inorganic compounds- for impregnation and coating of wood. A useful feature of ionic liquids is that they are both a vehicle for the impregnant while also having the ability to swell the polymer matrix.

Due to their high solvation ability for cellulose and small-molecular compounds, ionic liquids have been found useful as cleaning restoration agents for old paper artifacts by merely washing the material with an aqueous or alcohol solution of the ionic liquid. The degraded compounds from the paper artifact, which are the cause of yellowing or staining, are washed out, and the brittleness and toughness of the cellulose can be restored.

Chapter three presents a few case studies where ionic liquids can act as multipurpose additives to obtain multifunctional composite materials. Usually, multiple additives need to be compounded in a typical polymeric composite material for each required function (compatibilization, stabilization, etc.), but by using ionic liquids, multiple functions can be served by one the same compound. Ionic liquids act as good compatibilizers between thermoplastic polymer matrices and organic (wood, cellulose fibers) or inorganic reinforcing agents and fillers. At the same time, they provide water action resistance, UV stability, and function as biocides (i.e., fungicides).

Ionic liquids can serve as laser ablation media for graphite to obtain nanomaterials, such as multi-walled carbon nanotubes. They also improve nanomaterials' dispersibility and compatibility (e.g., multi-walled carbon nanotubes) with thermoplastic polymer matrices.

By exploiting ionic liquids' high solvation ability, composites comprised entirely of biopolymers can be obtained, resembling agglomerated wood panels without thermosetting polymers in the composition. A final application of ionic liquids presented in this chapter is related to obtaining composite aerogels comprised of a cellulose/palladium-on-carbon/ionic liquids structure. The composite materials show high hydrogen storage capacities at room temperature, making them viable candidates for energy storage applications.

Chapter four presents my research using ionic liquids as solvents and porogens for obtaining biopolymer hydrogels by a physical crosslinking method, namely the application of repeating alternate freezing and thawing cycles (cryogelation). The obtained hydrogels present good water stability and show a high sorption ability for heavy metals ions and dyes. Ionic liquids enable extending the cryogelation method to biopolymers, challenging to be dissolved otherwise in conventional solvent systems. Also, this chapter describes and models the behavior of poly (vinyl alcohol) hydrogels in an ionic liquid solution with various concentrations.

Future development of my (didactical) academic career is presented in **section B3**, alongside future research directions. The latter includes:

- synthesis of custom-made ionic liquids from "green" natural sources;
- assessment of the environmental and health impact of ionic liquids;
- extending ionic liquids' application to the obtaining of composites with other types of synthetic polymers besides polyolefins;
- application of ionic liquids in the valorization of polymer wastes, and
- synthesis of hybrid metal/ceramic coatings and films for photocatalytic applications.

My research activity has materialized in the publication of 38 papers with impact factor (indexed by Clarivate Analytics Web of Science) and 15 ISI-proceedings articles. I was project director for 3 research projects, and the visibility of my research is reflected by my h-index of 10 (Clarivate and Scopus). I am a full editor of the Journal of Materials Science (Springer, impact factor 3.553), and I am a reviewer of national projects financed by UEFISCDI.

(A2) Rezumat

Teza de abilitare intitulată *Materiale polimerice funcționale obținute cu lichide ionice cu rol de auxiliari și aditivi* prezintă rezultatele cercetărilor proprii, realizate după obținerea titlului de doctor în ingineria materialelor în anul 2010. Aceste rezultate se referă la obținerea, prelucrarea și aditivarea diferitelor materiale polimerice sintetice și naturale cu lichide ionice. Lichidele ionice reprezintă o clasă de compuși organici cu tensiune de vapori practic nulă (însemnând volatilitate scăzută), prezentând o aplicabilitate extinsă în diferite domenii, precum ingineria materialelor, energie, electrochimie, sau sinteza de materiale.

Informația prezentată în cadrul tezei de abilitare prezintă aplicabilitatea diferitelor lichide ionice ca agenți antistatici, stabilizatori împotriva radiațiilor UV și ionizante, agenți de curățare și de restaurare, solvenți sau agenți de transport în conjuncție cu diferite tipuri de materiale polimerice. Aplicabilitatea acestor compuși poate fi extinsă și în obținerea materialelor compozite cu matrice polimerică, a materialelor cu capacitate de adsorbție și stocare pentru hidrogen, precum și în cazul obținerii gelurilor polimerice cu capacitate de adsorbție ridicată pentru ionii metalelor grele și pentru coloranți organici. Ceea ce definește acești compuși este versatilitatea ridicată a acestora. Prin sinteză se pot obține lichide ionice cu diferite valori ale caracterului acido-bazic (Lewis), cu diferite stabilități termice, proprietăți electrochimice sau hidrofilie.

Rezultatele cercetărilor multidisciplinare sunt structurate în secțiunea B2 a acestei teze de abilitare în patru capitole: 1. *Aplicabilitatea lichidelor ionice în ingineria materialelor polimerice*; 2. *Lichidele ionice ca aditivi și auxiliari pentru materialele polimerice*; 3. *Materiale compozite cu matrice polimerică prin intermediul lichidelor ionice* și 4. *Geluri polimerice prin intermediul lichidelor ionice*. În încheierea tezei de abilitare sunt prezentate de asemenea elemente privind *Planurile de Evoluție și dezvoltare a carierei academice* (secțiunea B3).

Capitolul întâi prezintă elemente introductive referitoare la tipurile de lichide ionice, la importanța lor pentru domeniul ingineriei materialelor polimerice, precum și a avantajelor și limitărilor pe care le prezintă. De asemenea sunt trecute în revistă principalele aplicații ale lichidelor ionice în procesarea diferitelor materiale polimerice sintetice și naturale.

Capitolul al doilea prezintă rezultatele cercetărilor proprii referitor la aplicabilitatea lichidelor ionice în modificarea proprietăților materialelor polimerice. Sunt menționate exemple privitoare la capacitatea lichidelor ionice de a acționa drept stabilizatori UV și pentru radiația ionizantă a materialelor celulozice (fibre de celuloză, lemn). Materialele polimerice prezintă în general o afinitate crescută pentru acest tip de compuși. Efectul stabilizator-radioprotector al lichidelor ionice este direct proporțional cu capacitatea acestora de a se menține pe suprafața materialului polimeric (care depinde de asemenea de caracterul lor hidrofobic și de masa moleculară). Radiația ionizantă de tipul fasciculelor de electroni poate genera specii radicalice active în lichidul ionic, acestea putându-se grefa direct pe materialul polimeric. Datorită caracterului ionic, lichidele ionice pot fi utilizate ca și agenți antistatizanți pentru materialele polimerice, determinând o creștere a valorilor conductivității electrice de suprafață și o disipare eficientă a sarcinilor electrice acumulate.

Rezultatele cercetărilor proprii au indicat de asemenea că lichidele ionice pot servi drept plastifianți pentru materialele celulozice. Totuși, în contrast cu plastifianții tradiționali care determină o creștere semnificativă a alungirii la rupere pentru materialul polimeric dar și o scădere a rezistenței la rupere, lichidele ionice determină o creștere concomitentă a alungirii cât și a rezistenței la rupere a materialului. Acest lucru este posibil datorită rearanjamentelor macromoleculare pe care le promovează acești compuși în materialele polimerice.

O altă aplicație originală prezentată în acest capitol este legată de aplicabilitatea lichidelor ionice ca auxiliari, în speță solvenți pentru diferiți compuși naturali macromoleculari și mic-moleculari, precum și ca agenți de dispersie și transport pentru compuși anorganici în stare de pulbere, cu aplicabilitate în obținerea de acoperiri protectoare

pe lemn și în impregnarea lemnului. Lichidele ionice acționează ca solvent/agent de transport, determinând concomitent gonflarea lemnului, ceea ce facilitează pătrunderea impregnantului în structura acestuia.

Datorită capacității lichidelor ionice de a dizolva o gamă variată de compuși, este demonstrată aplicabilitatea acestora în curățarea/restaurarea artefactelor celulozice (hârtie veche), prin simpla spălare/umectare a materialului cu soluții apoase sau în alcool etilic ale lichidelor ionice. Compușii degradați/parțial degradați sunt solubilizați de către lichidele ionice, acestea determinând concomitent și o creștere a flexibilității și rezistenței mecanice a materialului.

Capitolul al treilea exemplifică prin prisma propriilor cercetări utilizarea lichidelor ionice ca aditivi cu funcțiune multiplă pentru materialele compozite. De regulă, pentru a conferi funcționalitate și proprietăți mecanice bune unui compozit este necesară adăugarea mai multor aditivi în receptura materialului (cu rol stabilizant, de compatibilizare etc.). Un lichid ionic adăugat în receptura materialului compozit poate îndeplini simultan atât rol de compatibilizator între agentul de umplere (lemn, fibre de celuloză, pulberi de natură anorganică) și matrice, cât și rol de stabilizant UV, sau rol de agent biocid (fungicid).

Tot în acest capitol este prezentată utilizarea lichidelor ionice ca medii pentru obținerea prin ablație laser a unor nanomateriale pe bază de carbon (nanotuburi multi-perete funcționalizate), cu compatibilitate ridicată față de matrice polimerice termoplaste.

Este redată de asemenea o aplicație legată de caracterul de solvent excepțional al lichidelor ionice pentru biopolimeri, anume obținerea compozitelor bazate integral pe polimeri naturali, fără adaos de rășini termoreticulabile. O ultimă aplicație prezentată în acest capitol este reprezentată de obținerea unor structuri poroase compozite de tipul aerogelurilor de celuloză, cu paladiu depus pe particule de carbon (Pd/C) și lichide ionice cu cation de alchilimidazoliu. Prezența lichidului ionic determină o capacitate de adsorbție și de stocare remarcabilă pentru hidrogen la temperatura camerei a acestor tipuri de materiale compozite.

Capitolul patru prezintă rezultatele cercetărilor proprii legate de utilizarea lichidelor ionice cu rol de solvenți și porogeni pentru obținerea de hidrogeluri din biopolimeri prin reticulare fizică (aplicarea de cicluri alternative de îngheț-dezghet, adică prin criogelare). Gelurile obținute prezintă o bună stabilitate în apă și o capacitate de adsorbție ridicată pentru ionii metalelor grele și pentru coloranții organici. Hidrogelurile din polimeri naturali sunt în general dificil de obținut datorită condițiilor restrictive în ceea ce privește solubilitatea acestora în solvenții uzuali. De asemenea, în acest capitol este prezentat, discutat și modelat comportamentul unor hidrogeluri tipice de poli (alcool vinilic) în soluții de lichid ionic de diferite concentrații.

Planurile de dezvoltare ale carierei academice pe plan didactic și de cercetare sunt detaliate în secțiunea *B3* a tezei de abilitare. Referitor la direcțiile de cercetare viitoare, acestea includ:

- sinteza unor noi lichide ionice "verzi", pornind de la compuși de origine naturală;
- evaluarea impactului de mediu și asupra sănătății a lichidelor ionice;
- extinderea aplicațiilor lichidelor ionice în obținerea de materiale polimerice cu alte tipuri de polimeri sintetici decât poliiolefinele;
- aplicarea lichidelor ionice în valorificarea deșeurilor de mase plastice;
- sinteza de acoperiri și filme hibride metal/ceramice pentru aplicații de fotocataliză.

Activitatea mea de cercetare până în prezent s-a materializat prin publicarea a 38 de articole cu factor de impact (indexate de Clarivate Analytics Web of Science) și a 15 articole în proceedings ISI. Am fost director de proiect pentru trei granturi de cercetare, iar vizibilitatea cercetărilor este reflectată de către indicii Hirsch 10 conform Clarivate și Scopus. De asemenea, sunt editor permanent al Journal of Materials Science (Springer, factor de impact 3,553) și sunt expert evaluator al UEFISCDI.

(B) Scientific and professional achievements and the evolution and development plans for career development

(B1) Professional achievements

In the following paragraphs, I will mainly emphasize my good background in materials engineering, the domain in which I wish to obtain my habilitation. Throughout my entire academic experience (2006-present), I have gained precious knowledge that enabled me to develop increasingly complex and innovative research in the domain of materials engineering, and I consider having utilized to good measure my background training (I graduated Physics and Chemistry in 2006 as valedictorian) in the materials' characterization.

The main goal of my Ph.D. study period between 2006 and 2010 (Chemistry Department of the Materials Science and Engineering Faculty from Transilvania University of Brasov) was to obtain and characterize novel molecularly-imprinted materials based on poly (vinyl alcohol), capable of selective separation of specific organic molecules from aqueous solution, of organic compounds purification, controlled delivery and selective adsorption of pollutants from wastewaters.

I disseminated the research in 4 papers indexed by Clarivate Analytics (ISI), 10 articles indexed in international databases (BDI), one book, and over 20 presentations at international conferences in the domain of polymeric materials engineering. Complementary with the Ph.D. stage program, in 2007, I won by competition my first research grant (Young Ph.D. Students, i.e., T.D., organized through competition at a national level by the National Council for Scientific Research in Higher Education, i.e., *CNCSIS*), entitled *Molecular imprinting studies of vinyl polymers applicable for selective separation of active principles*, which has enabled me to gain significant autonomy in additional financing my Ph.D. studies.

Throughout the Ph.D. studentship period, I was responsible for synthesizing and characterizing polymeric and inorganic oxide-based materials as a team member of several national and international research grants. I participated in two practical placements (in May 2008 and June 2009) at the Technical University of Istanbul, Turkey. At the Technical University of Istanbul, I participated in several conferences and thematic seminars in the domain of inorganic composites and experimental (obtaining and characterization) activities in cement matrix composite materials. During this period, I also participated in training sessions for several types of instrumental methods of materials characterization, such as fluorescence, FTIR and UV-VIS spectrometry, atomic absorption spectrometry, thermogravimetry, elemental analysis, and so forth.

In 2010, after finalizing the doctoral stage, I won a three-year postdoctoral grant (POSDRU) at the Product Design and Environment Faculty from the Transilvania University of Brasov, through which the primary core ideas that are contained in this thesis were crystallized.

The postdoctoral grant idea was to propose new alternatives to the processing of polymer materials (in particular, biopolymers), which could mitigate the disadvantages of traditional processing methods (high environmental footprint, tedious multi-step processing, and so forth) with the help of ionic liquids. These organic compounds could aid in more facile processing of polymers and impart new desirable properties to polymeric materials and composites. Another aim of my postdoctoral fellowship was to find alternative and environmentally-friendly recycling polymer waste methods (with emphasis on cellulose and lignocellulose) by using ionic liquids.

My didactical activity at the Transilvania University of Brasov throughout the 2006-2013 period was connexed to the domain of materials engineering and chemistry. I was responsible for teaching spectroscopic techniques of materials analysis, instrumental analysis, general chemistry, and physical chemistry in this period. In this

period, I was co-responsible (with my Ph.D. supervisor) of the Instrumental Analysis laboratory of the Product Design and Environment Faculty from the Transilvania University of Brasov. This period has enabled me to further specialize in spectroscopic methods of materials analysis (IR, NIR, fluorescence, UV-VIS, atomic absorption).

In the 2013-2015 period, I continued my collaboration with Transilvania University of Brasov as an associate assistant and lecturer, being involved at the same time in the research teams of several projects in materials engineering.

As associate teaching staff I was responsible for both didactic activities (laboratory, seminary, project, diploma, and dissertation thesis coordination) as well as coordinating students in research activities, in the framework of the scientific student's sessions. I also participating in elaborating new practical applications in the domain of spectroscopic materials characterization.

In 2015, I obtained a tenured lecturer position, respectively associate professor, starting from 2017, in the field of materials engineering at the Materials Science and Engineering Faculty from Transilvania University of Brasov. In this period, I was responsible for teaching Materials Science and Engineering, Materials Science and Technology, (in Romanian and English), Ecologic Materials for Welding at various university undergraduate and masterate programs. Also, I teach several disciplines related to research project management, means of protection for industrial radiations, and statistical process control to the undergraduate and masterate students from the Materials Science and Engineering Faculty.

During this period, I have won through competition two new projects and I have initiated research collaborations with the industrial environment:

- a) Young Research Teams, (Executive Unit for Financing Higher Education, Research, Development, and Innovation financing agency, i.e., *UEFISCDI*) regarding the use of ionic liquids as ecologic additives for polymeric composite materials, and
- b) an international project H2FC, financed through the FP7-INFRASTRUCTURES branch, regarding the synthesis and testing of novel ionic liquid-based hydrogen storage materials (Athens, Greece).
- c) a contract with Rom Waste Solutions SRL (Chiajna, Ilfov county) on determining the thermal, thermo-rheological behavior and density of polyolefin wastes (contract no. 10520/09.09.2016)

Since 2015 when I obtained a full tenured didactical position at the Materials Science and Engineering Faculty (Transilvania University of Brasov), I have attracted funds (through research grants for which I was director, through the funds granted by different internal competitions) to enlarge the materials study collection for the first year's Materials Science students, I have purchased new equipment and utensils for obtaining and characterization of polymer and polymer composite materials (mini extruder, molds, heated press, polarized transmission microscope, etc.). Also, I have enriched the existing didactical infrastructure related to the determining of different types of radiation and toxic gasses.

My ability to attract funds and organize independent research activities is demonstrated by obtaining research internships and grants through competition as director (two national grants, one international grant, and one postdoctoral internship).

My organizational-related skills and coordination ability stem also from the attracting of funds in the frame of research grants, coordinating young researchers and postdoctoral students (Young Research teams Project- PN-II-RU-TE-2014-4-0173), and coordinating students at their diploma and master thesis (since 2010, I have coordinated alone, or in collaboration, 20 undergraduate and 14 masterate students).

Also, since 2015, I am a member of the Department Council of the Materials Engineering and Welding Department from the Materials Science and Engineering Faculty, I participate yearly to the promotion of the Materials Science and Engineering Faculty undergraduate and masterate study programs, and I am a member in the Faculty Student Admission Committee. Since 2019, I am responsible for the Internal Managerial Control and Risks Assessment for my department (i.e., Materials Engineering and Welding).

The visibility of my research is demonstrated through the 53 papers indexed in ISI WoS (25 of which as first or corresponding author), the 230 citations in Clarivate Analytics ISI WoS and Scopus databases (h-index according to Clarivate ISI WoS and Scopus = 10), and my coopting as a reviewer for several journals.

From 2010, I have been involved in the peer review process for the following journals: *Materials Today Communications*, *Journal of Hazardous Materials*, *Applied Surface Science*, *Reactive and Functional Polymers*, *Materials Chemistry and Physics*, *Materials & Design*, *Water Research* (Elsevier); *Journal of Materials Science*, *Cellulose, Carbonates and Evaporites* (Springer Nature); *Journal of Wood Chemistry and Technology*, *Analytical Letters* (Taylor & Francis); *Journal of Applied Polymer Science* (Wiley); *Holzforschung*, *BioResources*, *Wood and Fiber Science*, *International Journal of Polymer Science*, *Current Analytical Chemistry*, *Acta Chimica Slovenica*, *Journal of Composite Materials*, *Journal of Mining and Metallurgy, Section B: Metallurgy, Polymers, Coatings* (also in the reviewer board for this journal), *Materials*, *Metals* (the last four of Mdpi).

My research coordinating abilities can be demonstrated through my coopting in several scientific committees of international conferences, as a reviewer for national projects and as an editor for scientific journals.

Since 2016 I was selected as a reviewer of national projects by UEFISCDI in the "Eco-nano-technology and advanced materials" and "New and emerging technologies" panels. Some grant competitions for which I have served as an expert reviewer, including the yearly and final grant reporting phases for the financed projects (a total of over 50 projects reviewed):

- PNCDI III, SP 2.1, Transfer to the economic operator projects (PTE-2019), Call year: 2019, Period of review activity: 2019
- PNCDI III, SP 2.1, Cheques of Innovation - CI-2018, Call year: 2018, Period of review activity: 2018
- PNCDI III, SP 1.2, Institutional development projects - Complex Projects realized in RDI consortia - 2017 Call, Call year: 2017, Period of review activity: 2017
- PNCDI III, SP 2.1, Cheques of Innovation - CI-2017, Call year: 2017, Period of review activity: 2017
- PNCDI III, SP 2.1, Transfer of knowledge to the economic agent „Bridge Grant”, Call year: 2016, Period of review activity: 2016
- PNCDI III, SP 3.5, EUREKA Network/ EUREKA Clusters 2016, Call year: 2016, Period of review activity: 2016

In 2019 I served as a Guest Editor for the *Materials Today: Proceedings* journal (ISI proceedings, Elsevier), and I was co-responsible for editing the special issue (Volume 19, Part 3, Pages 909-1098 (2019)) of the International Conference on Materials Science and Engineering (BRAMAT2019).

Starting from 2020, I am a Full Editor of the *Journal of Materials Science* (Springer, impact factor 3.553), founded in 1966 and established as one of the longest-standing journals in the domain of materials science and engineering. To present, I have evaluated over 400 papers for the journal.

An excerpt on accomplishing the criteria established by the Romanian National Council for Titles, Diplomas and Certificates (CNATDCU) for the *Materials Engineering* domain, as per Annex 7 of the Ministry of National Education and Scientific Research order no. 6129/20.12.2016 is presented in the table below. The minimum standards and the minimum scores for each category are accomplished and exceeded.

Crt. no.	Activity domain	Activity type	Categories and restrictions	Sub-categories	Minimal criteria (required)	Realized criteria
1	Didactic and professional activity (A1)	1.1 Books and chapters in specialty books in recognized publishers	1.1.1 Books / chapters as author	1.1.1.2 National: minimum 2, of which 1 as first author	2 books, of which 1 as first author	3 books, 2 as first author
		1.2 Didactic support	1.2.1 Manuals, monographs, including in electronic format: at least 2, of which 1 as first author		Minimum 2, of which 1 as first author	2 didactical manuals, 1 as single and 1 as first author
2	Research activity (A2)	2.1 Articles in ISI Thomson Reuters- Web of science Core Collection and ISI Proceedings indexed volumes	2.1.1 Minimum 15 articles, of which minimum 10 in ISI Th.R. (of which min. 5 with impact factor of min. 1, and min. 5 as main author with impact factor min. 0.5		15 articles, of which at least 10 in ISI-indexed journals, at least 5 as main author with impact factor min. 0.5	38 in ISI Th.R. journals, of which 34 with impact factor >1, and 25 as main author 15 in ISI proc.
		2.4 Grants/ research projects won by competition	2.4.1 Director/Partner responsible: Minimum 2, of which at least 1 as director		2 grants/ research projects, out of which at least 1 as director	3 research projects as director
3	Recognition and impact of activity (A3)	3.1 Citations in ISI Th.R. WoS Core Collection and other international indexing databases	Minimum 30 citations in ISI Th.R. WoS Core Colln and SCOPUS (without self-citations)			230 citations in ISI WoS
Synoptic table with scores on each activity domain						
Activity domain					Minimum required	Realized
Didactic and professional activity (A1)					60	87.10
Research activity (A2)					320	1515.02
Recognition and impact of activity (A3)					120	1379.95
TOTAL					500	2982.07

(B2) Scientific achievements

Chapter 1. Ionic liquids for the development of polymeric materials

This habilitation thesis presents the research results I have conducted in the domain of polymeric and composite polymeric materials obtained with a new class of organic additives called ionic liquids (ILs) after obtaining my Ph.D. title in materials engineering in 2010 granted through the Minister of Education and Research order no. 3492 from 23.03.2010.

1.1. Ionic liquids: features and limitations

The polymer processing industry often uses volatile organic solvents and additives for tuning the properties of the resulting material. Plasticizing agents (flexibility improvers), antistatic agents, lubricants, (thermal or radiation-related) stabilizers, biocides, and compatibilizers between different polymeric components in blends or between the matrix and reinforcing phase in composite materials are often employed. Many of these organic solvents possess non-negligible volatility, contributing to the atmosphere's pollution and bearing inherent potential toxicity to the biosphere.

Ionic liquids (also known as designer solvents, ionic fluids, or molten salts) are organic salts with melting points below or near 100°C at ambient pressure. To be liquid at room temperature, ILs must preferably present asymmetric cations (i.e., alkyl side chains with different sizes) (Qureshi et al., 2014). In liquid state (some from -80 to >300°C), these compounds are composed entirely of ions, as do, for example, molten inorganic salts, but at much lower temperatures. The main types of cations encountered in the structure of the most frequently used ILs are presented in Figure 1.1.

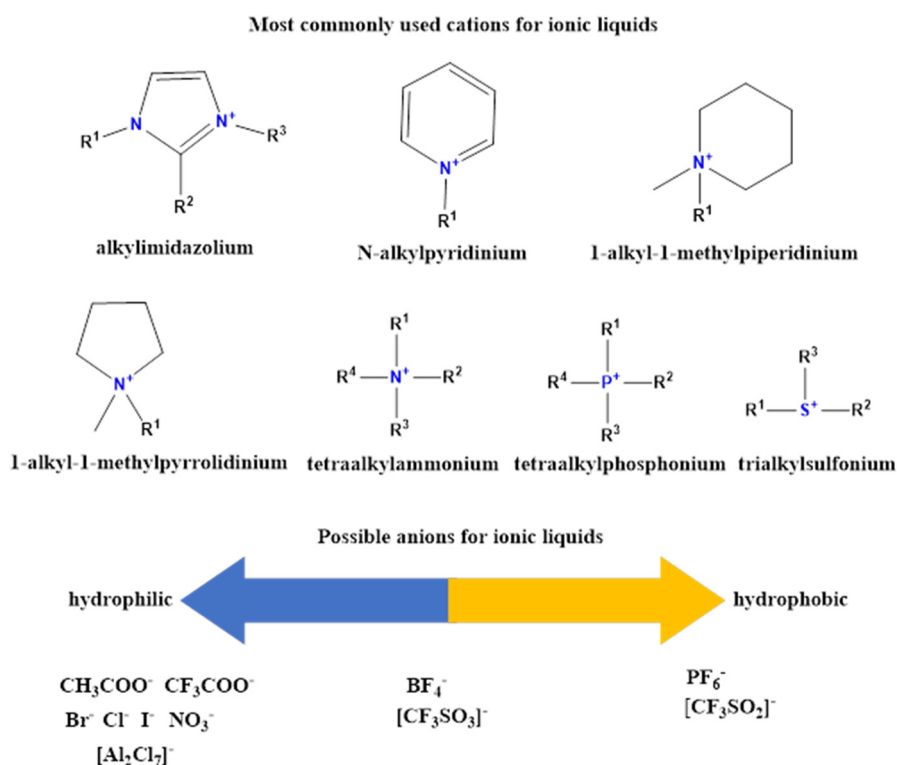


Figure 1.1. Possible cations and anions for ionic liquids (Croitoru and Roata, 2020)

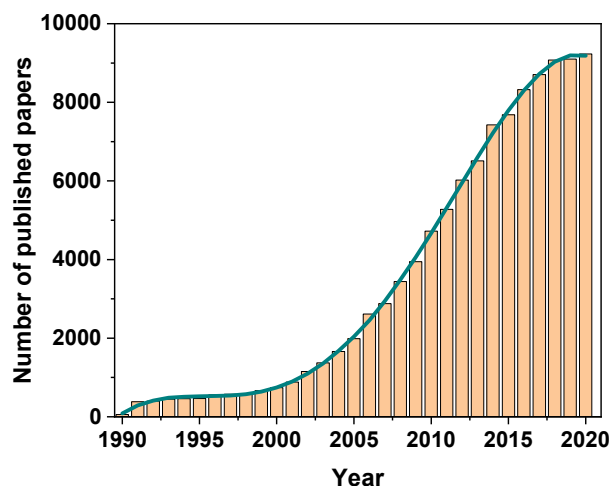


Figure 1.2. Dynamics for the yearly number of published papers related to ionic liquids (Clarivate Web of Science, accessed at 02.12.2020, search terms: “ionic liquids”)

The synthesis of an organic ionic liquid (ethylammonium nitrate) was reported for the first time in 1914 by Paul Walden (Plechko and Seddon, 2008). Since their first successful synthesis, ILs have not attracted much interest outside organic chemistry synthesis for almost nine decades. It was only since the early 90s with the development of alkylimidazolium ionic liquids that can dissolve cellulose and wood and be used as electrolytes in electrochemistry-related applications that boosted the research interest towards these compounds. Since 1990, a steady-state exponential yearly increase in the total number of papers has been registered, proving that the application domains for ionic liquids are still young and under continual development (Figure 1.3).

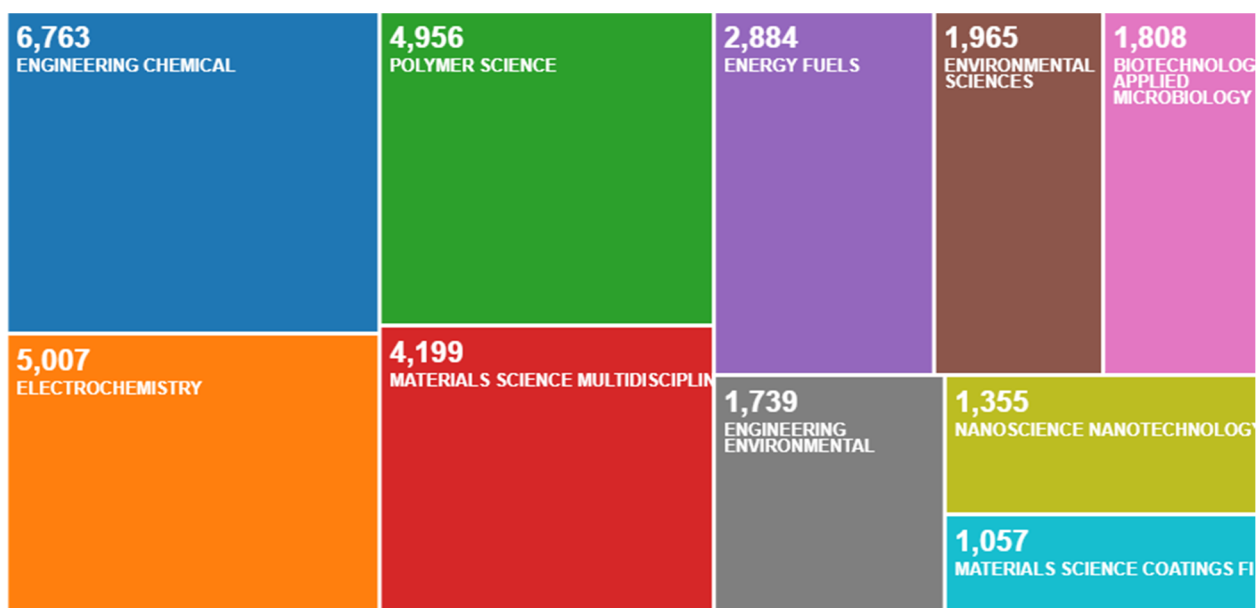


Figure 1.3. Visualization treemap for the application domains of ILs (Clarivate Web of Science, accessed at 02.12.2020, search terms: “ionic liquids”)

Ionic liquids are nowadays attracting much attention for applications in many fields of materials engineering and industry (Figure 1.3) due to their chemical stability, thermal stability, low vapor pressure (which means that basically, they have null volatility), non-flammability and high ionic conductivity properties (Lu et al., 2009). Over the last few years, ILs have increasingly been used as auxiliaries (solvents, porogens, and derivatization media) for organic materials synthesis, as catalysis, and as biocidal agents, plasticizers antistatic agents, both for synthetic polymers as well as for cellulosic biopolymers.

The combination of ILs with polymers enables the obtaining of functional polymeric materials, which can efficiently combine the features of specific polymers and ILs. Moreover, ILs can be modified to a great extent by incorporating functional groups with specific properties (hydrophilicity, biocidal effect, electrical conductivity, compatibilization between phases and their dispersibility, etc.) into the cation, anion, or both. Thus, it is possible to tune the IL, the polymer, or both to obtain a broad spectrum of multifunctional composites and address many applications' specific requirements (Correia et al., 2020).

Ionic liquids are expected to account for a total market share of 22 billion US dollars in 2022 as solvents and derivatization media. Their implementation in polymer-related applications is mainly hindered by their high cost. If in 2010, 1-ethylimidazolium chloride of 95% purity cost about €720 per kg, today the price has dropped to €335 per kg, and it is expected that it will continue to lower, as more large-scale companies will be involved in their mass production. To date, ionic liquids are produced industrially by Merck (Germany), Acros Organics (Belgium), TCI Chemicals (Japan), and IoLiTec (Germany), the latter one being specialized only in the synthesis of these types of compounds (Abushammala and Mao, 2020).

However, the results have indicated that ILs tend to have a much higher solvation ability than traditional polymer solvents and much higher derivatization potential for polymer materials, which could imply that higher amounts of materials can be processed in a single batch rather than in conventional applications. As additives for synthetic and natural polymeric materials, they can be added in low amounts, often diluted with water or other organic solvents.

Related to synthetic and natural polymeric materials, the roles and interactions promoted by ILs can be multiple, as detailed below:

- high solubility media for monomers, determining increased polymerization reaction rates, and:
- variable solubility towards synthetic polymers and copolymers, as depending on the molecular mass of the polymer, nature of the anion and cation of ILs and on the processing temperature (He et al., 2019);
- medium to high solubility for natural polymers: short-chain (<C₄) ionic liquids (especially those with 1-n-alkyl-3-methylimidazolium cation and chloride/acetate anion) present good cellulose (and other derived polymers, such as chitin, chitosan), wood and proteins dissolution ability (Meng et al., 2013).
- ILs can be used for polymers or biopolymers fractionation. For example, ionic liquids with long-chain side alkyl chains or aromatic substituents (especially when combined with bulky anions such as acetate or acesulfamate) are more selective towards aromatic polymers (such as lignin from wood biomass), possessing low cellulose dissolution ability. 1-ethyl-3-methylimidazolium formate is highly selective towards the dissolution of hemicellulose (Liu et al. 2019);
- as pretreatment media for wood biomass to improve the accessibility of the cellulase enzymes in the bulk of the wood (Hou et al., 2017);
- as media for polymers chemical modification, e.g., acetylation of cellulose in and 1-ethyl-3-methylimidazolium chloride/acetate mixture (Xie et al., 2007);
- as media for obtaining useful chemicals through depolymerization of synthetic or natural polymers. For example, ILs can be used as media to depolymerize poly (ethylene terephthalate) (PET) (Liu et al., 2020). Another chemical, 5-hydroxymethylfurfural, can be obtained after a long-run 24h thermal treatment of wood 1-ethyl-3-methylimidazolium chloride) (Dutta et al., 2017);
- as carriers for different impregnants or antifungal agents into the structure of porous polymeric and polymeric composite materials. In this application, ILs are useful through improving the penetration ability of the transported species through promoting polymer swelling (e.g., in the case of wood) (Croitoru et al., 2015a; Croitoru et al., 2015b);
- as plasticizers for polymers: ionic liquids with alkylammonium, alkylpyridinium, or 1-n-alkyl-3-methylimidazolium (>C₁₀) cations generally have low polymer dissolution ability, but can disrupt the inter- and intramolecular bonding and increase the number of amorphous domains in opposition with

the crystalline ones (Ou et al., 2014; Scott et al., 2010). ILs can be used to tune the flexibility and electrical conductivity of thermoset polymer network materials (Vashchuk et al., 2018);

- as additives, providing various functionality: fire retarders (especially alkylphosphonium ILs, or ILs with hexafluorophosphate or tetrafluoroborate anions) (Miyafuji and Fujiwara, 2020; Xu, 2010), thermal and UV stabilizers (Xue et al., 2018), antistatic agents (Tsurumaki et al., 2015), and compatibilizers (Shamsuri and Daik, 2015) for polymeric materials;
- as media for the obtaining of various (nano)particulate fillers for polymeric composite materials, including colloidal glasses and gels, lyotropic liquid crystals, nanoparticle-stabilized ionic liquid-containing nanoparticulate emulsions, ionic liquid surface-functionalized nanoparticles, and nanoscale ionic materials (He and Alexandridis, 2015).

1.2. Motivation behind the thesis

Despite the ongoing progress, the results reported so far still allow much work to be done in ILs applications in “green” polymer materials engineering, such as the ionic liquids’ structural and morphological impact on the resulted materials. The development of research in the field can significantly impact environmental protection efforts, optimize technological processes, and obtain materials with improved or new properties. Research in this field will also be the basis for developing of new theories on the interactions between ionic liquids and other types of substances such as polymers or obtaining new composite materials with functional properties, fields of utmost importance in both fundamental and applicative research domains for materials engineering.

I have started working in polymeric materials and ionic liquids due to the immense potential that these organic compounds could bring over traditional processing and additivating such materials. The use of ionic liquids with a relatively simple structure as surface polarity tuning agents for polymeric materials, UV stabilizers, functionalization media, compatibilizers in composite materials with organic polymer matrix, carriers, and solvents for the obtaining of polymer gels and composite materials has been relative less researched comparing to the application of ILs related to cellulose biomass dissolution.

My research aimed to respect as much as possible the principles of “green polymeric materials” obtaining and processing, namely “less hazardous synthesis,” “benign solvents and auxiliaries,” and “prevent waste” (Sandhu and Sandhu, 2011). These original research results related to polymeric materials engineering are structured in the next three chapters of the habilitation thesis, citing the appropriate publication. The full list of these publications can be found in the *bibliography* section with my name bolded out. For a complete overview of the research ideas in this domain, I have also included some non-published material (data and pictures from my research archive).

Nevertheless, on a secondary plane of view, the motivation behind this material's writing lies in taking the next step of the academic career, namely my including in the doctoral school of the Transilvania University of Braşov and tutoring of Ph.D. students in the field of materials engineering.

Chapter 2. Ionic liquids as additives and auxiliaries for polymeric materials

2.1. Ionic liquid additives and auxiliaries: synopsis and motivation

The production of synthetic polymers and the processing of biopolymer materials has increased manifold over the last 60 years due to their inexpensive, durable, and lightweight nature (Sazali et al., 2020). These characteristics have exponentially determined the growth in the demand for polymeric materials. However, on the other hand, they have created several challenges related to the auxiliaries (solvents, carrier media, dispersing agents) and additives (e.g., plasticizers, lubricants, stabilizers, antistatic or biocidal additives) that are conventionally used in their obtaining or processing (Hahladakis et al., 2018). Despite the usefulness of these additives and auxiliaries for polymer materials processing and polymer products, most of them have a non-negligible potential to contaminate soil, air (e.g., the volatile organic compounds, i.e., organic solvents), or water and can lead to harmful human exposure (Hansen et al., 2013).

Despite synthetic polymers' performance, one of the principles of sustainable development states that environmental strainers such as synthetic polymers should be replaced when possible with potential alternatives derived from renewable materials, i.e., biopolymers (Mahmood and Moniruzzaman, 2019). Biopolymers, derived from natural resources typically exhibit closed-loop life cycles as an integral part of a future materials' industrial ecology.

Concerning biopolymers (cellulose and natural or artificial modified celluloses, wood-based lignocellulose, and so forth), there is a sort of "shortlist" for additives or auxiliaries in contrast to synthetic polymers due to their high molecular masses and intricate tertiary structure built up from inter- and intramolecular bonding. A broad category of biopolymers can be conventionally processed only under relatively demanding conditions (use of potentially toxic organic solvents, highly corrosive acid, or alkaline mixtures, and so forth) that have a negative influence on the performance and the structure of the processed material (e.g., by molecular weight changes and structural modifications) as well as a pronounced environmental footprint (Dassanayake et al., 2018; Niaounakis, 2015).

Ionic liquids have proven as suitable auxiliaries (solvents) for most biopolymers (cellulose and wood-derived lignocellulose being the most widely researched) due to the disruptions they promote in the inter- or intramolecular bonding of these materials. They easily enable biopolymer extraction, functionalization, and obtaining advanced biopolymeric materials more facile (Naz and Uroos, 2020; Tan and MacFarlane, 2009).

They have also proven useful as additives for tuning various properties of biopolymer materials (surface energy, compatibility with other types of materials, stabilizers, and so forth) (Lins et al., 2015; Zavgrodnaya et al., 2015).

Since starting my postdoctoral internship in 2010 (contract number POSDRU/89/1.5/S/59323), I was continuously focused on researching new application for ionic liquids (as carriers, solvents, or additives) in the processing of biopolymers, with a focus on cellulose, wood, and wood-derived lignocellulose. My research aimed to extend the ionic liquids' applicability potential and provide new insights into their mechanism of interaction with various polymer systems.

In my research, I have demonstrated the suitability of ionic liquids as UV-stabilizing agents for wood and cellulose fibers (Croitoru et al., 2011a; Patachia et al., 2012), as beta-radiation stabilizers for wood (Croitoru et al., 2014), as antistatic and surface-tuning agents for wood and cellulose (Croitoru et al., 2011a; Croitoru et al., 2011b), plasticizers (Croitoru et al., 2011c; Patachia and Croitoru, 2013. Croitoru and Roata, 2021), and as antifungal agents for wood (Croitoru et al., 2018a; Croitoru and Roata, 2020).

I have proven the suitability for alkylimidazolium based ILs to provide heterogeneous-phase grafts on cellulose nanofibers for improved compatibility with, e.g., synthetic polymers (Croitoru and Patachia, 2016).

Also, I have demonstrated that alkylimidazolium the ionic liquids could be useful as solvents for other types of biopolymers (chitin, chitosan, proteins, coniferous resins, etc.), and carriers for inorganic compounds in obtaining "green" protective coatings on wood and in wood impregnation (Croitoru et al., 2011d; Croitoru et al., 2015a; Croitoru et al., 2015b; Patachia and Croitoru, 2016, Croitoru, 2018). This idea has led to obtaining two patents in the domain of ecologic wood impregnation (Croitoru et al., 2016; Patachia et al., 2016).

Even if, technically, wood should be regarded as a natural polymeric matrix composite, I will present my research results in conjunction with wood in this chapter.

2.2. Ionic liquids as stabilizers for cellulosic materials

Cellulose is the most abundant biopolymer on earth. Cellulose and lignocellulose (wood) have been used since ancient time for clothing, paper making and packaging or as construction material (Kamel et al., 2008).

It is well known that under outdoor use, cellulosic materials (textile fibers, paper, wood-based products, and coatings) when exposed to direct or diffuse sunlight, moisture, and temperature variations, undergo rapid weathering which has a negative impact on their properties (dramatic loss of mechanical strength, yellowing, hydrophilicity increase and so forth) (Urreaga and de la Orden., 2006).

The exposure to sunlight (especially the UV part of the solar spectrum) is one of the determinant factors that negatively affect the performances of cellulosic materials, especially in the presence of impurities, such as traces of metal ions, dyes, delustrants and so forth (Lam et al., 2011; Urreaga and de la Orden, 2006).

There are relatively few studies concerned in UV photoprotection of cellulosic materials, among which wood is the most often subject. Wood is usually protected by UV-absorbing coatings (hindered aromatic amines) or by impregnation with chromium-arsenate salts, which are toxic and present an environmental risk (Cristea et al., 2010; Zervos, 2007).

Studies regarding the photoprotection textile materials and paper have employed the use of acrylic polymer-based coatings, dyeing, silane-based polymers grafting on partially oxidized cellulose or impregnation with chitosan or alginates, unfortunately with very little long-term efficiency (Gambichler et al., 2002).

Using ionic liquids as environmentally friendly and chemically stable UV protecting agents for cellulosic materials represents an important research direction, both for theoretical and practical points of view.

2.2.1. Ionic liquids as UV stabilizers for cellulose

I have tested the suitability of several alkylimidazolium liquids as UV-protecting agents for cellulose. The results regarding 1-ethyl-3-methylimidazolium chloride (EMIMCl); 1-ethyl-3-methylimidazolium hexafluorophosphate (EMIMPF₆), and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) ionic liquids are presented in this subsection, as these have yielded the most satisfactory results in this direction.

The ionic liquid-treated cellulose has been submitted to UV (254 nm) irradiation for 50 hours, and several analytical techniques were used to evaluate the occurring structural modifications. The use of low wavelength radiation decreases the necessary time to evaluate the surface changes and offers pertinent information regarding the effectiveness of the protection agent in terms of preserving the initial structure and surface chemistry of the material. Short UV wavelength irradiation could also serve to assess the occurring modifications under the worst possible degradation scenario.

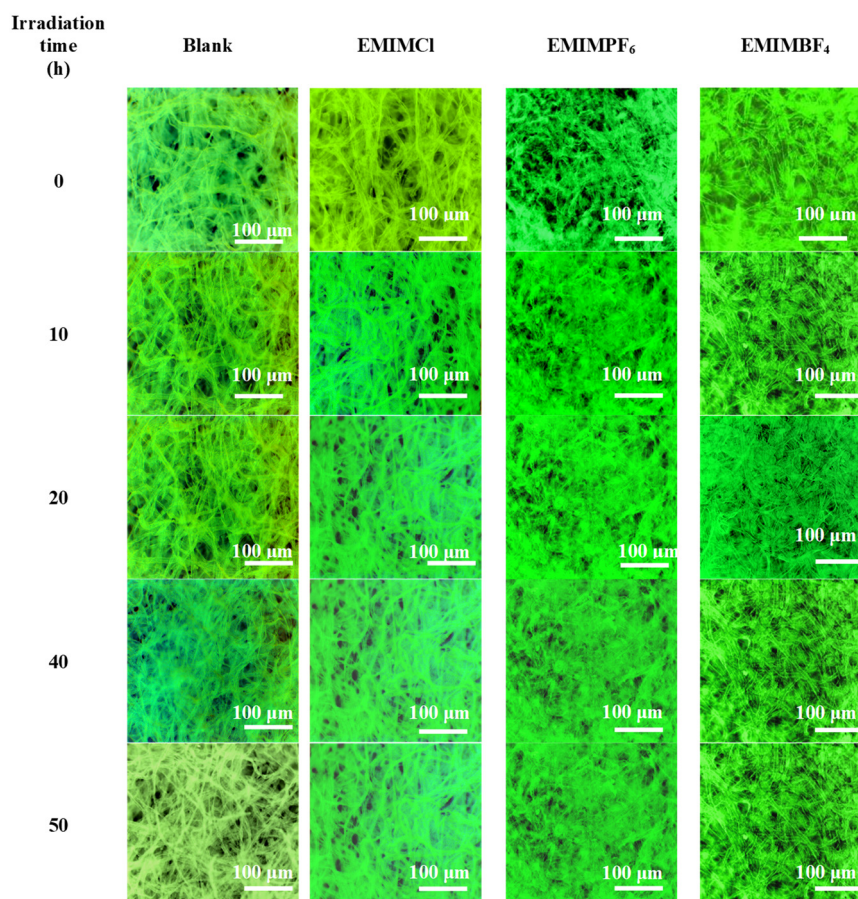


Figure 2.1. Fluorescence microscopy images of cellulose treated with ionic liquids after different UV exposure period (Croitoru et al., 2011a)

In cellulose treated with ionic liquids, it can be observed from the fluorescence microscopy images (Figure 2.1) that swelling has occurred. Also, a compaction of the fibers occurred in IL-treated cellulose compared to the blank sample, probably due to more favorable structural rearrangements of the macromolecular assembly.

Several structural parameters from the FTIR spectra of the cellulose and IL-treated cellulose materials submitted to UV irradiation were calculated (Figure 2.2). Studies on cellulose degradation have proven that weakly bonded water plays an essential role in oxidation and chain scission reactions (Gumuskaya et al., 2003). The ratio between the bands' areas at $\sim 1639\text{ cm}^{-1}$ and at 2900 cm^{-1} has been calculated. This ratio is often recalled as moisture index (MI).

The height ratio of the bands at 1371 and 2900 cm^{-1} has been used to determine the crystallinity index (CrI) of cellulose and the advantage is that it can be applied to both cellulose I and II (Gumuskaya et al., 2003; He et al., 2007).

The lateral order index (LOI) was calculated by using the ratio of the band heights at 1430 and 898 cm^{-1} , which is related to the proportion of cellulose I from the sample (He et al., 2007).

It has been found that native cellulose is a mixture of two crystalline modifications (cellulose I_{α} and I_{β}) that vary in proportion, depending on the cellulose source. In bacterial cellulose, the I_{α} (triclinic) form dominates, while in higher plants, I_{β} (monoclinic) is predominant (Gumuskaya et al., 2003; Sturcova et al., 2004).

The ratio of cellulose I_{β} to I_{α} (allomorph index, AI) has been calculated as the height of the band at $\sim 708\text{ cm}^{-1}$ (ascribed to I_{β}) divided by the height of the weak band at $\sim 751\text{ cm}^{-1}$ (ascribed to I_{α}) (Marin et al., 1999). This allomorph index, in addition to the crystallinity index and moisture index offers important information related to the structural rearrangements in cellulose when in contact with the ionic liquid or when irradiated with UV.

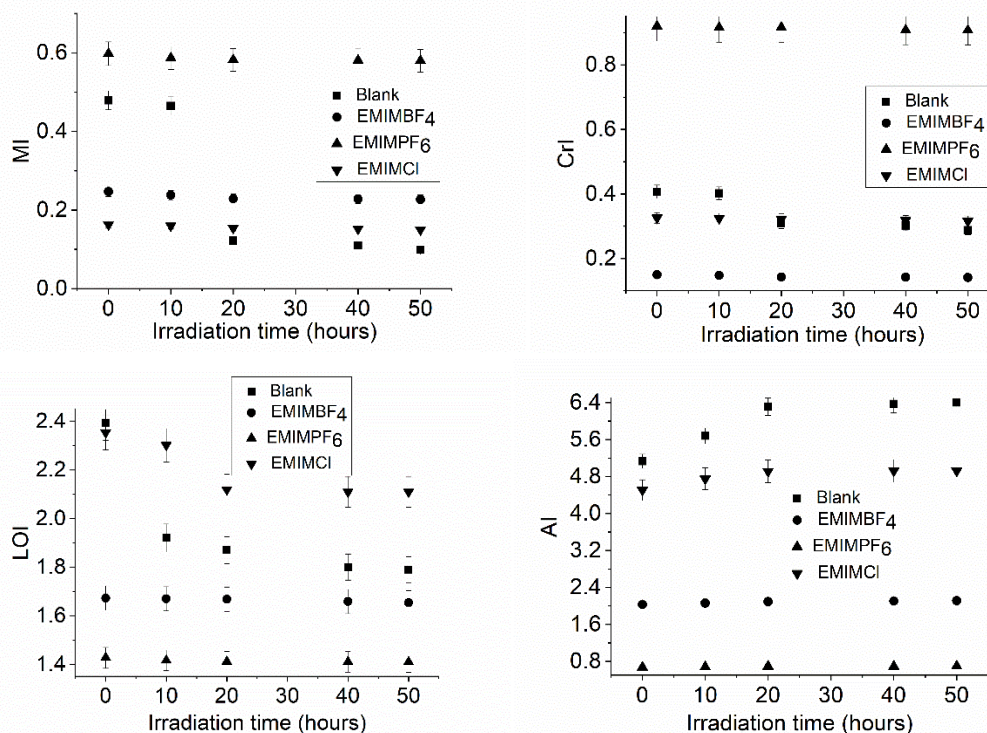


Figure 2.2. Structural parameters calculated from the FTIR spectra of UV-irradiated cellulose: moisture index (MI), lateral order index (LOI), crystallinity index (CrI) and allomorph index (AI) (Croitoru et al., 2011a)

The data from Figure 2.2 shows that a decrease of the moisture index with up to 80% of the initial value has been observed for irradiated blank cellulose. A more pronounced MI decrease during UV exposure could indicate a higher degree of degradation. During UV irradiation of the blank cellulose sample, the transformation of cellulose I to II (more stable) has been observed from the decrease of the LOI values. A lower LOI is associated with a higher cellulose II content, increasing stability to UV exposure. A decrease in the LOI values (relative content of cellulose I) (with up to 50% in the case of cellulose treated with EMIMPF₆, even if the amount of absorbed EMIMPF₆ was the lowest from all the three ILs used) in favor of the cellulose II polymorph has been shown to occur also in the ionic liquid treated samples, in comparison with the untreated sample, which could be associated with increased stability to UV irradiation.

A decrease in the CrI has been observed for the blank irradiated cellulose sample, starting from 10 hours of UV exposure, probably due to chain scission and oxidation reactions. Researches regarding the crystallinity of cellulose II have proven that generally, cellulose II has a lower CrI than the original cellulose I from which it was obtained. Also, cellulose II is more thermodynamically stable than cellulose I and more resistant to chemical treatments. This could explain the stabilization effect that ILs seem to have on the cellulose fibers under UV irradiation.

During UV irradiation of the blank cellulose sample, an increase in the AI has been observed starting from 10 hours of UV exposure, due to the transformation of the I_α to the I_β form, more thermodynamically stable.

The lower values of the AI in the case of IL treated cellulose (with up to 90%, in the case of EMIMPF₆) in comparison with neat cellulose indicate a conformational transition of cellulose I from the I_β to I_α allomorph form.

Even if the I_β form is the thermodynamically stable one, and results from the I_α form during annealing, the latter is more mechanically resistant and rigid, due to the tighter packing of the cellulose macromolecules (shorter hydrogen bonds) (O'Sullivan, 1997). For cellulose treated with EMIMPF₆ (the highest I_α content) a higher CrI has been recorded compared to the other IL treated cellulose, in addition with the increase of the I_α fraction.

Generally, it is admitted that the I_{α} allomorph is more chemically reactive (O'Sullivan, 1997), which could explain the high yields of functionalized cellulose when using ILs as solvents.

It has been reported by other researchers (Asako et al., 1987) that high yield of I_{α} can be produced starting from I_{β} by various solid-state chemical reactions.

For the cellulose treated with ILs, lower variation in the crystallinity, lateral order, moisture, and allomorph indexes with irradiation time (2-20%), in comparison with the blank cellulose sample has been recorded, owing to the stabilization effect that ILs seem to have on cellulose exposed to UV. The best UV stabilizing effect has been registered in the case of using 1-ethyl-3-methylimidazolium hexafluorophosphate ionic liquid.

2.2.2. Ionic liquids as UV stabilizers for wood

I have also assessed alkylimidazolium ionic liquids' suitability as UV stabilizers for wood under accelerated UV exposure (254 nm). As model wood materials, poplar (*Populus L.*) veneers were treated at the surface with four types of alkylimidazolium-based ionic liquids: 1-butyl-3-methylimidazolium chloride (BMIMCl); 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), 1-hexyl-3-methylimidazolium chloride (HMIMCl) and 1-dodecyl-3-methylimidazolium chloride (DMIMCl).

The photographic images of ionic liquid treated veneers and reference exposed to 254 nm UV radiation as a function of time are presented in Figure 2.3.

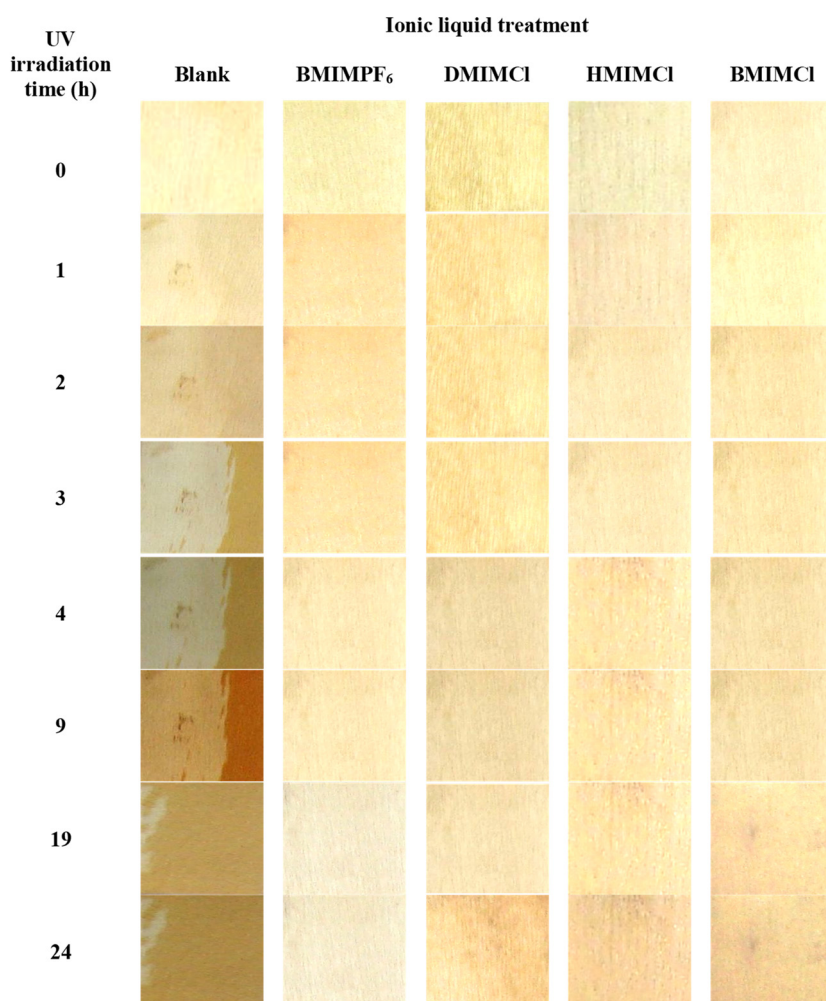


Figure 2.3. Photographic images of ionic liquid treated veneers and reference exposed to 254 nm UV radiation as a function of time (Patachia et al., 2012)

The UV radiation has a negative impact on the color of the wood. For the untreated (blank) sample, rapid darkening and significant overall color changes occur, starting from the first 60 min of UV exposure, rendered by rapid degradation of lignin from the wood's surface. It has also been noted that the irradiated wood became brittle, and the surface exfoliated easily in comparison with the non-exposed one.

It was observed from the FTIR spectra of the irradiated wood samples that the ionic liquid treatment is effective in enhancing the lignin stability to UV exposure. The characteristic aromatic lignin band at $\sim 1507\text{ cm}^{-1}$ decreased up to 10% of its original value in case of unprotected wood. Moreover, the lignin decay is combined with strong formation of new bands in the region below 1700 cm^{-1} (conjugated and aromatic chromophore carbonyls or quinones).

As for cellulose in subsection 2.1.1, several parameters were calculated from the FTIR spectra, namely the lignin index (LI) and the carbonyl index (CI), which are given in Figure 2.4 as a kinetic.

The lignin index of the wood was calculated for all the non-treated and ionic-liquid treated samples as the ratio between the height of the lignin-characteristic band at 1507 cm^{-1} (specific for lignin) and of the band from 893 cm^{-1} (ascribed to C (1)-H stretching from cellulose) (Temiz et al., 2005). The band's intensity at 893 cm^{-1} is not influenced by lignin, is very stable to oxidation, and remains constant throughout the wood exposure to UV light (Muller et al., 2003).

Similarly, the carbonyl groups index (CI) is calculated as the ratio between the band's heights at 1730 cm^{-1} and 893 cm^{-1} (Grelier et al., 1997).

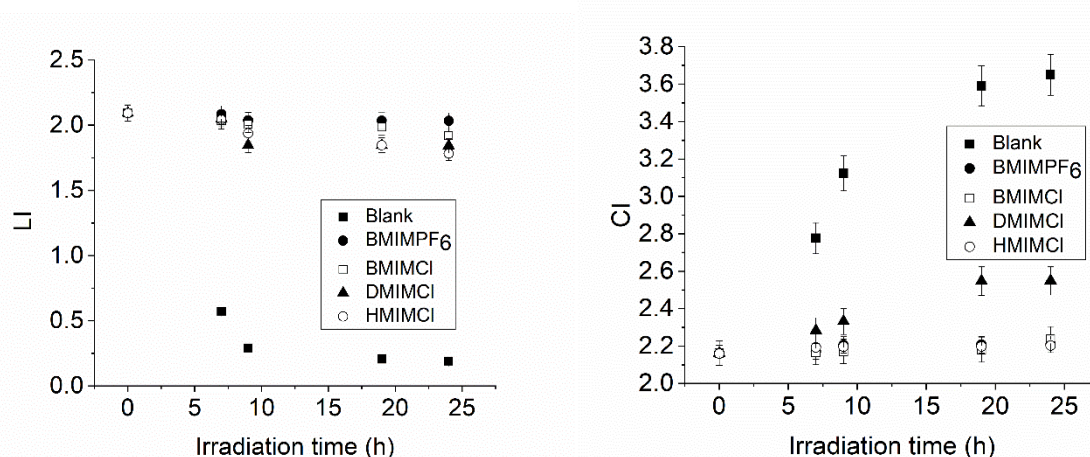


Figure 2.4. (left): Lignin index variation with the irradiation time for the IL-treated veneers and blank; (right): Carbonyl index variation with the irradiation time for the IL-treated veneers and blank (Patachia et al., 2012)

The ionic liquid treated veneers presented overall lower lignin and carbonyl index variations than the blank veneer, which could mean that the ionic liquid acts as a protection agent for lignin, reducing its UV light decay by blocking the formation of quinones, carbonyls, or peroxides. Since the studied ionic liquids are optically transparent in the 240-800 nm domain, the photostabilization occurs mainly due to interfering with the lignin degradation mechanism rather than acting as UV screens.

The results have indicated that ionic liquid treatment seems to stabilize the wood's surface color during UV irradiation, as little modification in overall color is observed. The surface coloring of wood can be directly linked with the proportion of lignin in the material. When this chromophore aromatic compound suffers structural damage, this is readily deduced in the darkening or yellowing of the wood's surface.

The most effective of the studied ionic liquids seems to be 1-butyl-3-methylimidazolium hexafluorophosphate, probably because its higher viscosity and lower affinity to wood determine its preferential distribution on the surface of the veneers.

2.2.3. Ionic liquids as electron beam radiation stabilizers for wood

Electron-beam (EB) irradiation is a commonly used technique to sterilize wood, enhance its chemical reactivity towards different compounds, initiate in-situ polymerization of impregnating monomers, or in grafting compounds to the reactive hydroxyl groups of cellulose.

The EB irradiation method's advantage as a tool to modify wood properties consists in its short processing times and the absence of toxic and expensive reactants. However, wood may be subjected to irreversible (and often undesired) chemical and structural modifications. Modifications could include lignin degradation, which leads to discoloration, cellulose oxidation, and chain scission, leading to low mechanical properties), negatively affecting wood's usability and overall life cycle (Czvikovszky, 1996).

Following a similar methodology for studying the UV-stabilizing effect of ILs, I wanted to study the impact of electron-beam irradiation on the surface properties of wood treated with ionic liquids to conclude if they could function as electron beam stabilizers as well.

Tangentially-cut sycamore maple (*Acer pseudoplatanus*) veneers were treated with three imidazolium-based ionic liquids, namely 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), and 1-hexyl-3-methylimidazolium chloride (HMIMCl). All the IL-treated materials have been subjected to electron-beam irradiation at the Electron Accelerator Laboratory from the National Institute for Lasers, Plasma and Radiation Physics, Bucharest ALIN-10 electron linear accelerator (6.23 MeV energy, 100Hz beam impulse). The EB dose rate was established at 2.4 kGy/minute to finally accumulate 50 kGy at the end of the exposure period.

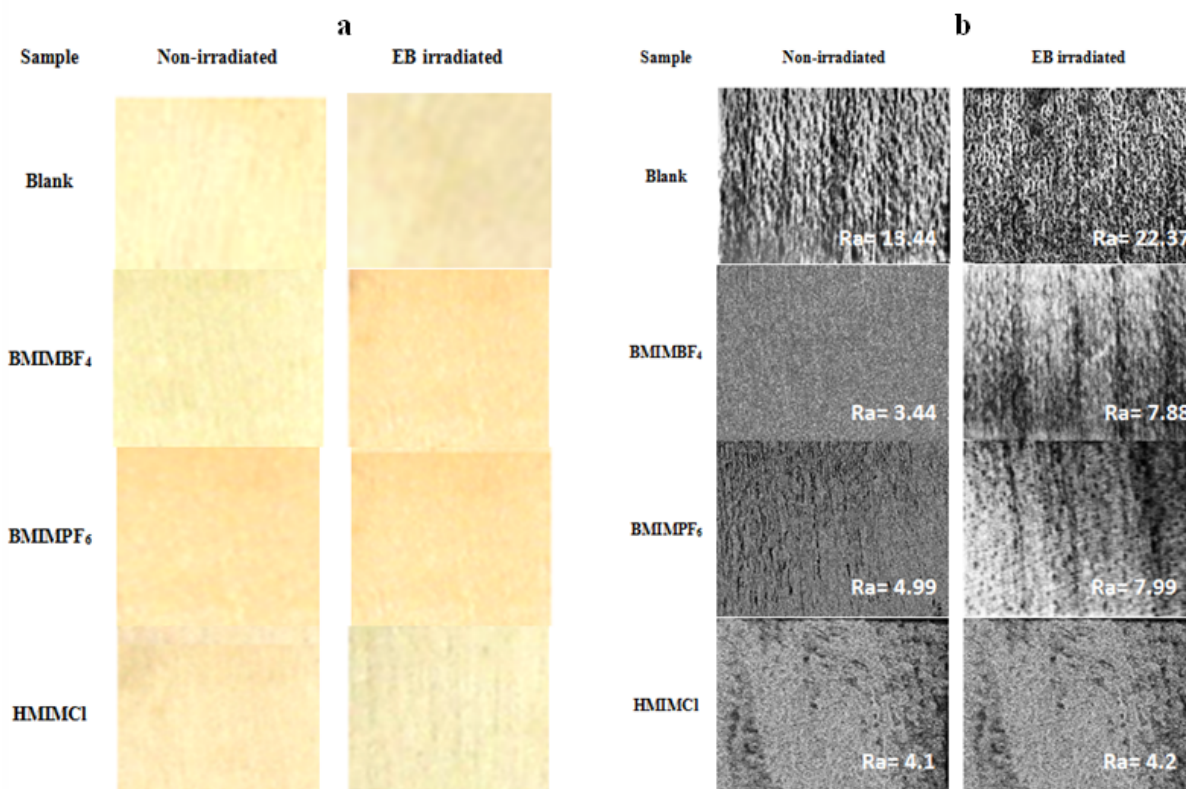


Figure 2.5. Photographic images (a) and roughness profile images (b) of EB irradiated and non-irradiated wood veneers treated with ionic liquids and blank (Croitoru et al., 2014)

The experimental results have indicated that the ionic liquid treatment determines better preservation of the structural features of wood (cellulose crystallinity and lignin concentration on the surface) as well as its surface properties (surface energy, roughness, color) upon irradiation with the electron beam, in comparison with the

reference wood (Figure 2.5 and 2.6). To assess the structural modifications that occurred in the irradiated wood and eliminate the interference from the ionic liquids' overlapping bands, the ILs were washed from the material with methanol. The removal of ILs has been monitored by measuring the electrical conductance of the washing liquid and through monitoring the decrease of the absorption bands specific to ILs from the spectra of the materials.

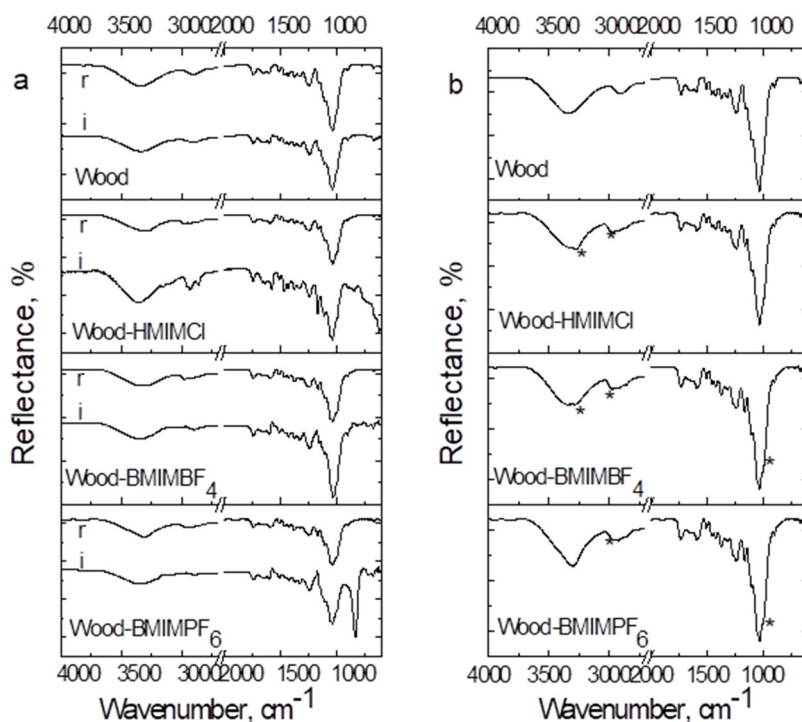


Figure 2.6. FTIR spectra of (a): irradiated (i) and non-irradiated (r) ionic liquid treated wood and reference; (b): irradiated wood after ionic liquid removal and reference wood (Croitoru et al., 2014)

It can be seen from the FTIR spectra in Figure 2.6a that the ionic liquid treatment enhances the lignin stability to EB exposure at the surface of the samples. The relative reduction in the intensity of the lignin characteristic band at $\sim 1507\text{ cm}^{-1}$ is less pronounced than in the untreated wood. A lower relative decreasing in cellulose crystallinity index by comparing the IL-treated samples (i) with the non-treated reference (r) could be observed.

As far as the information obtained from the FTIR spectra is concerned, it seems that the most efficient protection agent for wood against structural damage due to electron beam irradiation would be BMIMPF₆. Its mechanism of action may dominantly imply the inhibiting the propagation of free radicals involved in cellulose and lignin degradation and its preferential degradation, rather than that of the wood. The other ionic liquids may protect wood due to their preferential degradation on EB irradiation instead of wood and in inhibiting the propagation of free radicals, but in a lesser manner than BMIMPF₆.

The FTIR spectra of irradiated IL-treated wood from which the IL was removed with methanol (Figure 2.6b) indicate the presence of a weak shoulder at $\sim 3010\text{ cm}^{-1}$ in the alkyl-stretching region, possibly assigned to the vibration of C (2)-H bond from imidazolium ring. Supplementary, the FTIR spectra of the irradiated and washed wood initially treated with HMIMCl and BMIMBF₄ present a distinct -OH stretching vibration mode from that of wood and EB-irradiated wood at $\sim 3200\text{ cm}^{-1}$, which may indicate the presence of a hydroxylated imidazolium ring graft.

It could be possible that under the highly energetic electron beam treatment, the imidazolium free radicals (or the hydroxylated imidazolium cationic radicals) react with the -OH groups from cellulose, forming aromatic imidazolium-derived ethers (Figure 2.7). The occurrence of a shoulder at $\sim 1270\text{ cm}^{-1}$ in the irradiated and washed

wood samples (Figure 2.6b) may indicate the formation of a possible new ether-specific bond between the -OH groups of cellulose and the IL that seems to confirm the structure schematically represented in Figure 2.7. Etherification of wood with imidazolium ILs could be useful in moisture-stabilizing the material, or in imparting several functional properties to it, such as antifungal character, tunable surface polarity, and so forth.

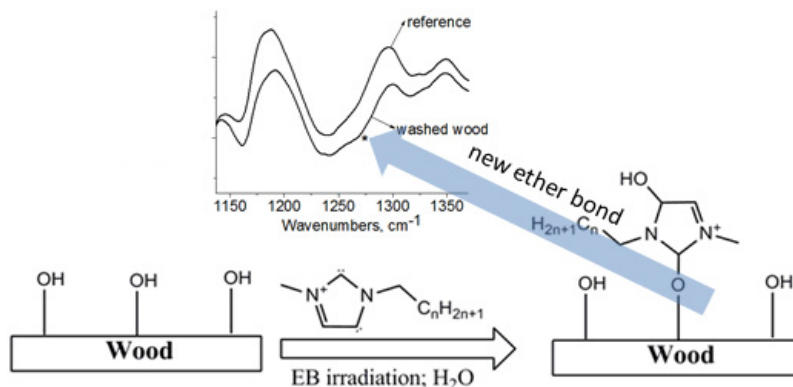


Figure 2.7. Possible mechanism of imidazolium grafting to wood (Croitoru et al., 2014)

AFM phase imaging of irradiated wood from which the ionic liquid has been removed by washing with methanol has revealed the presence of a “grainy” surface with higher roughness than the original or IL-treated wood. This may be accounted by the possible covalent-bonding of imidazolium-derived moieties to the partially-swollen cellulose microfibrils from the surface of the wood under high-energy EB irradiation (Figure 2.8).

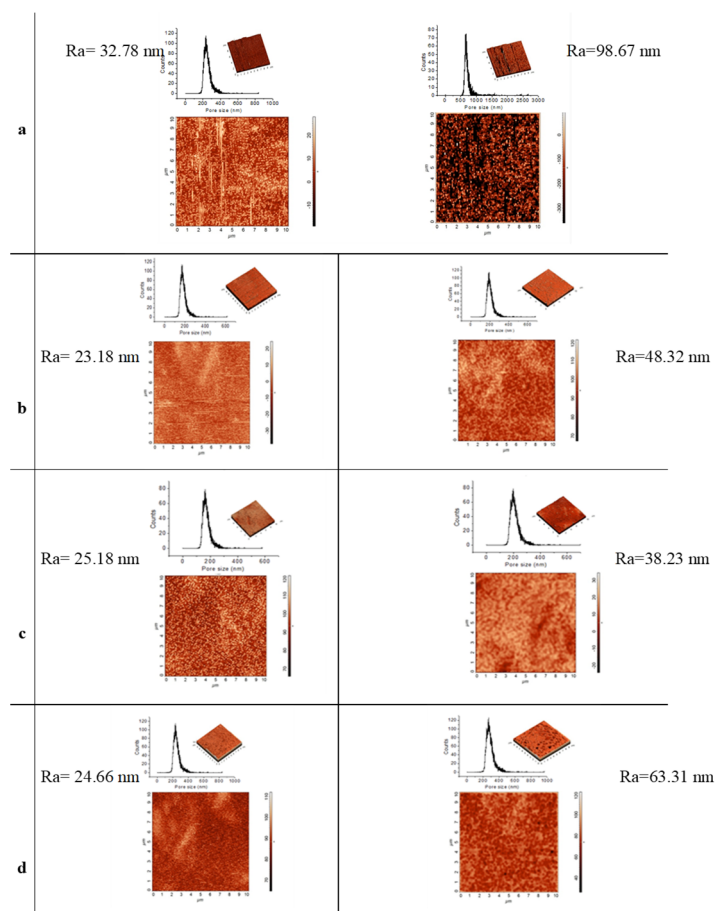


Figure 2.8. AFM phase, 3D images, pore distribution and roughness of: (a)-left: wood; right: irradiated wood; (b): BMIMBF₄, (c): BMIMPF₆, (d): HMIMCl-treated wood- left; right: irradiated wood after IL removal (Croitoru et al., 2014)

Both BMIMBF₄ and BMIMPF₆ seem to promote 'grain-like' imidazolium-derived moieties on the wood's surface, practically the same average dimensions (180 nm). HMIMCl is expected to form many covalently bound moieties with higher average dimensions (260 nm), due to its higher instability to irradiation. Since the dimensions of the imidazolium moieties are higher than the average diameter of BMIM⁺ (46 Å) and HMIM⁺ (69 Å) cations (Fletcher et al., 2002), it is suggested that such formations may occur by the association of neighboring imidazolium moieties. This association could occur through hydrogen bonds (imidazolium ring) or van der Waals interactions (lateral alkyl chains), or several of them could also possibly represent swollen wood microfibrillar structures.

2.3. Ionic liquids as antistatic agents for cellulosic materials

Generally, studies on cellulosic materials properties modification with ionic liquids' help seem to focus on ILs with complicated structures, which are very expensive and make their influence on materials structure and properties challenging to quantify (Pernak, 2000).

Most studies are conducted to study ionic liquids' influence on cellulose materials' bulk properties rather than surface properties. There are only a few studies concerning the modification of wood surface properties with imidazolium-based ionic liquids (Li et al., 2004).

I studied the influence of ILs on the surface properties of wood on poplar (*Populus sp.*) veneers treated with four types of imidazolium-based ionic liquids, namely 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄); 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), 1-butyl-3-methylimidazolium chloride (BMIMCl), and 1-butyl-3-methylimidazolium tetrachloroferrate (BMIMFeCl₄) (Figure 2.9). This research direction aimed to assess the antistatic effect of the ILs through surface electrical conductivity, contact angle, and surface energy measurements compared to the untreated wood (Croitoru et al., 2011b).

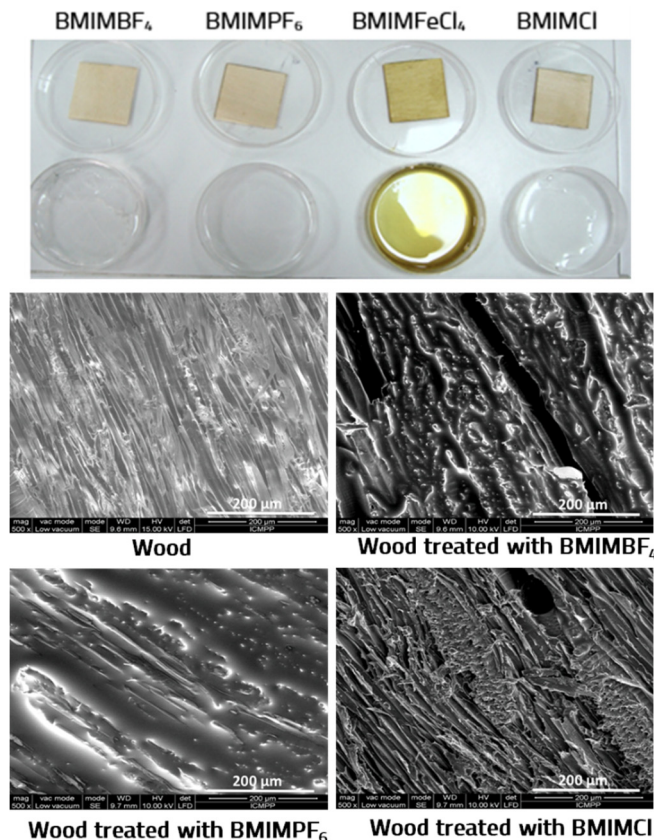


Figure 2.9. Photographic images and surface SEM microscopy images of the wood samples treated with ILs (Croitoru et al., 2011b)

The electrical conductivity measurements were made by using the four-point method. The experimental setup included a Jandel Universal Probe measurement stand connected to a Keithley 6221A DC/AC current source and a Keithley 2182 nanovoltmeter. All conductivity measurements were performed at 22°C.

For the evaluation of the electrical conductivity, Eq. 2.1 was used:

$$\rho = \frac{1}{\sigma} = 2\pi s \frac{V}{I} \quad (\Omega \cdot \text{cm}) \quad (2.1)$$

where σ denotes the electrical conductivity, s is the spacing between the needle-shaped sensors in cm, I is the test current and V is the measured voltage.

It is widely recognized that wood wettability and surface free energy are useful parameters that provide information on the interaction between adhesives or coating materials and the wood surface (Wolkenhauer et al., 2009). I have measured the wooden veneers' surface energy through contact angle measurements using the sessile drop technique.

The wood samples' surface energy has been calculated using the Lifshitz-van der Waals and Lewis Acid-Base (LW/AB) approach. According to this approach, the surface energy (γ) is decomposed into a Lifshitz-van der Waals (γ^{LW}) dispersive component as well as into a polar component - γ^p - with Lewis acid (γ^{p+}) and Lewis base (γ^{p-}) contributions respectively (Eq.2.2) (Rudawska and Zajchowski, 2007):

$$\gamma = \gamma^{LW} + \gamma^p = \gamma^{LW} + 2\sqrt{\gamma^{p+} \cdot \gamma^{p-}} \quad (2.2)$$

The initial contact angle θ_0 , which is the contact angle at the beginning of the wetting process ($t = 0$) for the test liquids, was used to calculate surface energy.

As shown in Table 2.1, the total surface energy of untreated and treated wood veneers ranges within 43–64 mN/m, and it is mainly due to the LW component.

Except for the case of BMIMPF₆ ionic liquid, which is hydrophobic and imparts lower surface energy to wood, the veneers' treatment with ionic liquids seems to improve their surface wettability remarked by higher surface energies and lower initial contact angles for water by comparing to the untreated sample.

Table 2.1. Surface energies of the ionic liquid treated samples (Croitoru et al., 2011b)

Ionic liquid treatment	$\theta_{0\text{water}}$ (degree)	γ (mN/m)	γ^{LW} (mN/m)	γ^p (mN/m)	γ^{p+} (mN/m)	γ^{p-} (mN/m)
Blank	36.85	43.66	37.64	6.02	1.21	7.48
BMIMBF ₄	32.34	46.97	41.06	5.91	0.15	59.83
BMIMPF ₆	56.75	45.51	34.52	10.99	1.02	29.50
BMIMFeCl ₄	28.29	63.15	44.14	19.01	1.91	47.28
BMIMCl	17.36	63.37	39.10	24.27	3.39	43.48

Also, it could be noted that the dominating contribution to the polar component of the surface energy is the Lewis base one, which means that the treated veneers surfaces have electron-donor properties. As the BF₄⁻, PF₆⁻, FeCl₄⁻ and Cl⁻ anions are known to present electron-donor ability (Pitula and Mudring, 2010), it is suggested that these anions remain on the surface of the wood during treatment, as revealed by the SEM micrographs of the respective wood veneers from Figure 2.9). The imidazolium cations could preferentially interact with the cellulose-lignin matrix of wood.

The electrical conductivities for ionic liquid treated and untreated veneer samples are presented in Table 2.2, alongside the amounts of ionic liquids absorbed into the wooden veneers after 15 min of immersion. The affinities of wood for the ILs with BF₄⁻, PF₆⁻ and FeCl₄⁻ anions is relatively similar, demonstrated from their higher uptake values, while the chloride IL is absorbed in the highest amount.

Table 2.2. Electrical conductivities of wooden veneers and amounts of ionic liquids absorbed (Croitoru et al., 2011b)

Ionic liquid treatment	σ (mS/cm)	$m_{IL\ abs}$ (g)/g wood
Blank	0.002	-
BMIMBF ₄	0.53	0.2437
BMIMPF ₆	0.64	0.2312
BMIMFeCl ₄	0.58	0.2417
BMIMCl	1.11	0.4750

BMIMBF₄ determines the lowest electrical conductivity from the series of ILs studied, probably due to its ability to extract bonded water from the wood structure, which dilutes the ionic liquid, decreasing the electrical conductivity. BMIMFeCl₄ absorbed amounts are lower than for BMIMBF₄, but it determines a higher conductivity of wood, probably due to the compounds resulting at FeCl₄⁻ hydrolysis (HCl high mobility). BMIMPF₆, being hydrophobic and more viscous than the other types of ILs, is maintained at the veneer's surface and generates higher conductivities.

Ionic liquids are non-volatile and chemically-stable compounds; they could be considered useful as ecologic surface treatment agents for wood. The definition of anti-electrostatic capability varies among different industries but generally agrees with ASTM D 991-00. So, articles with electrical conductivities in the range of 10⁻⁴ to 10⁻⁶ S/cm will exhibit anti-electrostatic properties (Li et al., 2004). The electrical conductivities obtained for the poplar veneers using simple immersion in ILs are higher than those reported in the literature up to this date (Cieniecka-Roslonkiewicz et al., 2005). Furthermore, this simple immersion method does not involve any additional treatment of the samples, and uses cheaper ionic liquids. ILs with hydrophobic cations can be better retained in the structure of the wood, as they are more resistant to leaching than conventional antisatic agents (inorganic salts solutions).

2.4. Ionic liquids as plasticizers for cellulosic materials

Treating cellulose fibers or wood through soaking in alkylimidazolium ionic liquids with low cellulose dissolution ability has proven successful in plasticizing cellulose materials. Typical ILs with plasticizing effect on cellulose include 1-dodecyl-3-methylimidazolium chloride and tetrafluoroborate, 1-ethyl-3-methylimidazolium tetrafluoroborate, and respectively hexafluorophosphate (in concentrations up to 5% wt. in ethanol, or 1:1 vol. water: ethanol mixtures) (Croitoru et al., 2011c; Croitoru and Roata, 2021).

Figure 2.10 synthetically illustrates the results obtained regarding the value of strain and tensile strength at breaking point for lignocellulose fibers impregnated with various types of ionic liquids (0.3 g/g dry fiber loading). Concomitant with a significant increase in the strain (due to cellulose chains flexibilization, i.e., plasticization), a significant increase in the tensile strength was also reported (due to structural rearrangement of cellulose, i.e., disruption in the inter- and intramolecular hydrogen bonds, followed by rearrangement in a more compact and stable configuration).

The increase in strain and tensile strength deems ionic liquids useful in obtaining cellulose fibers or wood with better processability, flexibility and anti-wrinkle ability (for fibers) (Croitoru et al., 2011b).

All fiber material was conditioned to 6% equilibrium moisture content in a dessicator containing suprasaturated Mg(NO₃)₂ solution before performing the tensile mechanical tests. The tensile tests were performed at a strain rate of 0.5 mm/s.

The coding corresponding to the ionic liquids' cations are as follows: EMIM: 1-ethyl-3-methylimidazolium; BMIM: 1-butyl-3-methylimidazolium; HMIM: 1-hexyl-3-methylimidazolium and, respectively, DMIM: 1-dodecyl-3-methylimidazolium.

It can be seen from Figure 2.10 that the increase in fiber elongation at break follows the order $\text{EMIM}^+ < \text{BMIM}^+ < \text{HMIM}^+ < \text{DMIM}^+$ for ionic liquid cations, in order of their increasing molecular mass (the so-called "spacer effect", illustrated in figure 2.11).

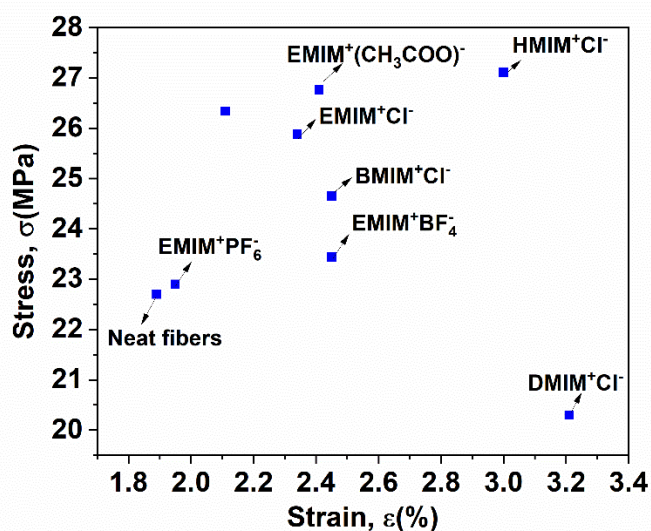


Figure 2.10. Tensile performance of cellulose fibers treated with imidazolium ionic liquids (Croitoru et al., 2011b; Croitoru and Roata, 2021)

The anions also present a "spacer" effect, determining various plasticizing effects for the same cation, but their effect is also due to their ability to interact with cellulose. Conversely, the tetrafluoroborate and the chloride anions present the highest plasticizing ability, as opposed to hexafluorophosphate, which normally presents the highest ionic volume among the three anions.

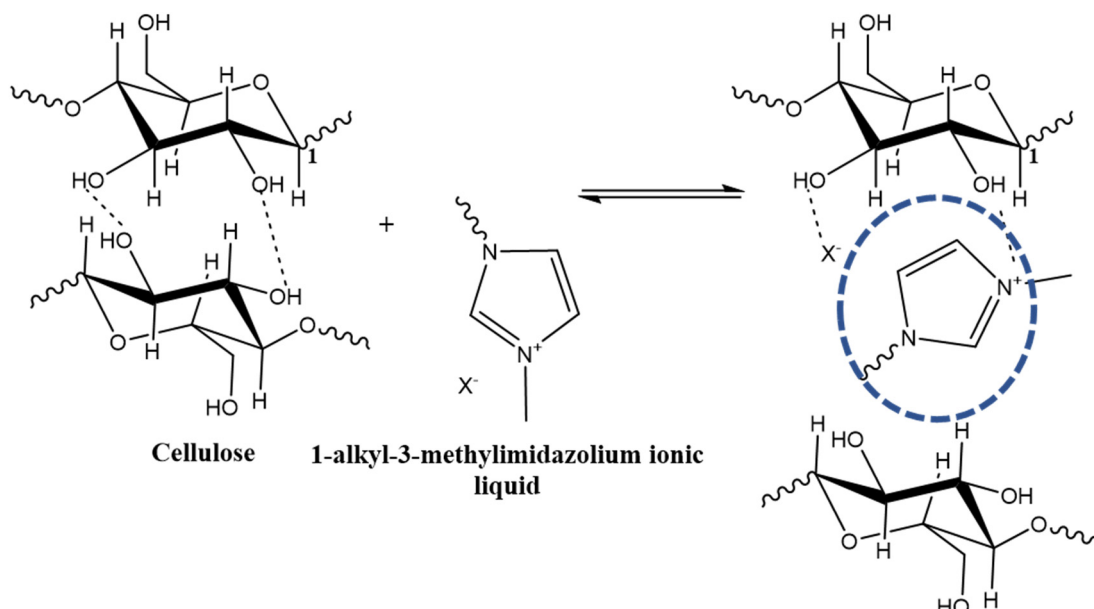


Figure 2.11. Illustration of the ILs plasticization effect on cellulose (Croitoru and Roata, 2021)

The counterion has an essential influence on the tensile properties. Experimenting with different types of ionic liquids has proven that polar hydrophilic cations (Cl^- , CH_3COO^-) have a markedly influence on the fiber's tensile strength, due to their ability to potentiate macromolecular rearrangement. Dominatingly hydrophobic anions

(such as PF_6^- or BF_4^-) tend to have a more dominating influence on strain values, acting as conventional plasticizers via the “spacer” effect (Croitoru et al., 2011b).

Generally, the spacer effect is proportional to the ionic volume of the anion, with bulkier anions being more effective plasticizers.

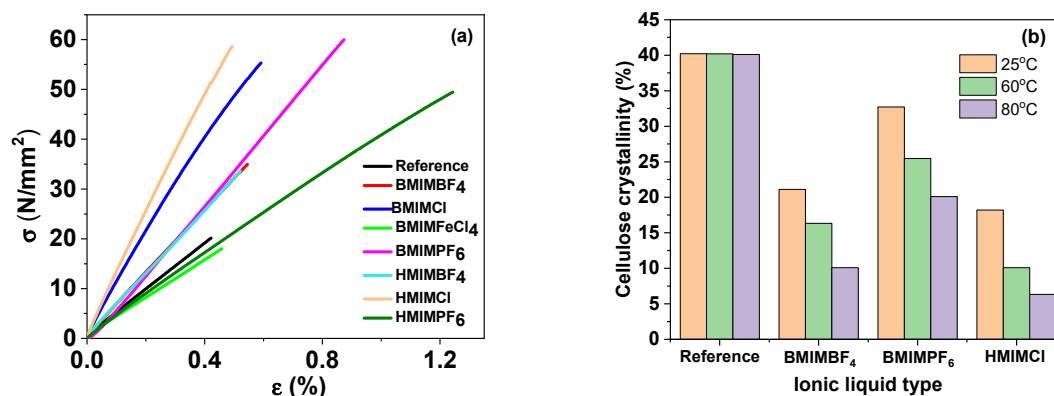


Figure 2.12. Illustration of the ILs plasticization effect on wood: (a) stress-strain curves; (b) dependence of cellulose crystallinity with temperature (Croitoru et al., 2011c)

For wood, ILs have the same dependency of the plasticization effect with the IL cation size (Figure 2.12a). The plasticization effect is markedly increased with the increase in temperature, evidenced by the decrease in the crystallinity index of cellulose determined from the corresponding XRD spectra (Figure 2.12b) (Croitoru et al., 2011c).



Figure 2.13. Photographic images illustrating the plasticization of wood by HMIMCl (POSDRU/89/1.5/S/59323 postdoctoral experimental report, 2011)

Treatment of wood with ionic liquids enhances the flexibility and the forces necessary to shape the wood material. Once deformed, IL-treated wood maintains its deformed shape more readily (the IL facilitates the disruption in the inter- and intramolecular bonds between the macromolecular components of wood) compared to untreated wood (Figure 2.13).

2.5. Ionic liquids as antifungal agents for wood

One of the most efficient methods for fungal attack prevention of wood (aside from chemical functionalization, impregnation with synthetic resins or coating methods, e.g., painting) is represented by the passive or pressure impregnation of different types of preservatives (Laks, 2008). Historically, oil-based preservatives (including those containing polycyclic aromatic hydrocarbons) were among the first used, followed by waterborne preservatives based on silicates, borates, fluorides, heavy metal ions salts (especially Zn^{2+} and Cu^{2+}), metallic or

metal oxide particulate dispersions, metal-heterocyclic compounds complexes, or salts of arsenic/arsenous acid (Stirling and Temiz, 2014). These formulations generally represent efficient antifungal formulations in terms of considerably extending the lifecycle of wood end-products on a mid or long-term level but possess significant shortcomings such as relatively high toxicity (aside from silicates and some borates), and a moderate to high leaching potential (Croitoru and Roata, 2020).

To date, there are less than thirty research papers related to the use of IL as antifungal agents for wood (not counting those related to cellulose and paper), which is very few, considering the high synthesis versatility of this class of compounds (there are mainly nine types of "conventional" organic cations, with a practically unlimited choice of anions). The advantages of using ILs as preservatives reside in their excellent absorption and fixation into the wood's structure without altering its texture or color.

To enrich the database in the use of ILs as fungicide additives, I have tested the potential antifungal character of two ionic liquids: methyltrioctylammonium bis (trifluoromethylsulfonyl)imide (MTOIm) and trihexyltetradecylphosphonium bis (2,4,4-trimethylpentyl) phosphinate (TTDPP). The screening method chosen to assess the antifungal character of the ILs has been determined was adapted from Delenk et al. (Delenk et al., 2015). For this procedure, a volume of 200 μ L from each ionic liquid was pipetted to culture media prepared in standard Petri dishes (100 mm diameter) with 1.5% agar and malt extract, previously autoclaved at 121 $^{\circ}$ C for 20 min. The ionic liquids were uniformly spread on the surface of the culture media with a sterilized spatula.

The inoculation has been performed after 24 hours in a central position of the plate, using *Postia Placenta* (brown rot, a typical fungus that attacks and decomposes cellulose in wood). The samples were incubated at 23 \pm 2 $^{\circ}$ C temperature and 75 \pm 5% humidity. An agar plate with the same type of fungus was inoculated without any biocide as a reference to observe the fungus' natural growth. The fungal growth was observed periodically at determined time intervals (3, 7, and 11 days after inoculation) and qualitatively assessed by photographic image analysis of the fungus development in the culture media (Croitoru et al., 2018a).

The potential antifungal characters of the two ionic liquids incorporated in the fungus growth media, in comparison with the reference culture media is depicted in Figure 2.14, against brown rot (*Postia placenta*).

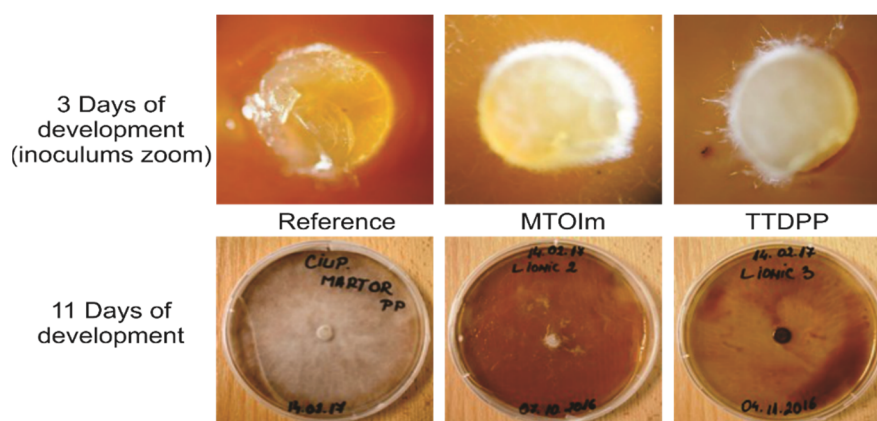


Figure 2.14. Photographic images of fungal development in IL-containing media and reference (Croitoru et al., 2018a)

It could be seen that after 3 days of inoculating, the fungus strain presents approximately the same development growth both on ionic liquids-containing media, as well as in the reference agar media. After this short incubation period, differences in fungus growth could be noted: in the reference culture media, uninhibited growth of fungus could be noted, as the mycelium grows radially outward starting from the inoculum point, covering the entire culture media after 11 days of incubation. In the case of both MTOIm and TTDPP ionic liquids, interference with the mycelium development could be clearly evidenced.

It could be concluded that brown rot fungus growth could be inhibited through using low amounts of the two ionic liquids, imparting fungicide and/or fungistatic character to the composite materials.

2.6. Ionic liquids as functionalization media for cellulose nanofiber materials

Surface treatment of cellulose nanofibers (CeINF) via physical or chemical modification methods is important to tailor CeINF surfaces for application in specific polymer matrices, both in compatibility and controlling their aggregation. Several studies have been performed regarding the surface modification of cellulosic nanofibers through grafting to the cellulose -OH groups of low-polarity moieties via organic (acrylates, anhydrides, chlorotriazines and their derivatives, isocyanates, monomers, and so forth) or hybrid organic-inorganic (silanes and titanates) functionalization agents (Espino-Pérez et al., 2014). Many of these functionalization agents require the use of volatile organic solvents (dichloromethane, toluene) and initiators, which possess an environmental risk due to their volatility and toxicity.

I have developed an alternative method of cellulose nanofibers functionalization through low temperatures (25-35 °C) surface modifying of cellulose nanofibers with long-chain imidazolium cationic moieties. The fibers' treatment is achieved by simple immersion of the cellulosic material in beta-irradiated 1-hexyl-3-methyl-imidazolium tetrafluoroborate (HMIMBF₄) ionic liquid. The particularity of using this ionic liquid is that it swells and plasticizes the cellulose fiber without dissolving it. Plasticization and swelling aid in a more efficient functionalization of the cellulosic material.

The nanofibers were obtained through controlled hydrolysis in an acidic medium, starting from cotton linters. This cellulose source (linters) was preferred, due to its high cellulose content, high purity, and availability as a byproduct of the textile industry.

Electron beam exposure experiments of the HMIMBF₄ ionic liquid has been performed at the Electron Accelerator Laboratory from the National Institute for Lasers, Plasma and Radiation Physics, Bucharest, with the ALIN-10 electron linear accelerator (6.23 MeV energy, 100 Hz beam impulse). The β radiation dose rate has been 2.4 kGy/min, to finally accumulate 50 kGy at the end of the exposure period (Croitoru and Patachia, 2016).

The CNFs, separated from the distilled water have been placed in the irradiated ionic liquid, in stoppered glass vials, so as the ratio of cellulose to the irradiated ionic liquid to be 1:10 % wt. The treatment involved magnetic stirring of the CeINF-IL system for 24 h at two temperatures, namely 25°C and 35°C. After ionic liquid treatment, the cellulose nanofibers have been washed several times with ethanol and distilled water to remove any traces of non-bonded ionic liquid from their structure. The IL removal was assessed by repeated electrical conductance measurements of the washing liquid.

The EB radiation at doses of 50 kGy is responsible for imidazolium ring scission, especially at C(2)-H and C(5)-H in the imidazolium ring, as determined from our previous research (Croitoru et al., 2014). This ring scission could be accounted for the formation of free radicals and imidazolium oligomers, but more important for this study, hydroxylation of the imidazolium cation in the presence of trace amounts of absorbed water.

The FTIR spectra of the irradiated IL-treated CeINFs (Figure 2.15) present some particularities, namely, the overall shifting of all the main characteristic absorption bands to lower wavenumbers, associated with the flexibilization of the cellulose macromolecular architecture, due to the conversion of the cellulose I anomer, possessing higher crystallinity, to the dominating amorphous cellulose II anomer. The shift is more pronounced with the increasing in the EB-irradiated IL treatment temperature.

For the IL-treated CeINF fibers at 35°C, an increase in the relative intensity of the alkyl stretching bands centered at 2859-2893 cm⁻¹ with 97%, concomitant with the relative decrease in the intensity of the -OH stretching bands at 3120-3350 cm⁻¹ (with 44%) was observed from the analysis of the corresponding FTIR spectra (Figure 2.15). Also, the appearance of a weak shoulder at 3122 respectively 3148 cm⁻¹ (ascribed to H-C(4) and H-C(5) vibration from the imidazolium ring) was noted.

These structural modifications could be ascribed to the grafting of carbonyl groups bearing simple or (poly)hydroxylated imidazolium moieties on the nanofibrillated cellulose material's surface, possibly through

hemi(acetal) or ether bonds, respectively. From these two possible linkage modes (acetal or ether), acetalization is the most probable because of the milder required reaction conditions. Possible new acetal/ether bonds also appear as weak shoulders centered at 1060 cm^{-1} and at 1516 cm^{-1} owing to the weakly acidic pH of the EB-irradiated IL (~ 5.8). Also, the presence of the bands from 1579 cm^{-1} , attributed to plane C–C and C–N symmetric and asymmetric stretching of the imidazole ring from the IL could serve as a possible supplementary indication of CeINFs functionalization (Chowdhury and Thynell, 2010).

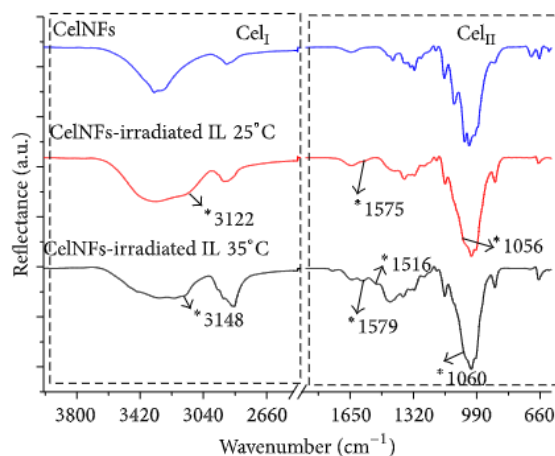


Figure 2.15. FTIR spectra of CeINFs obtained with irradiated IL at 25°C and 35°C (Croitoru and Patachia, 2016)

After ionic liquid treatment, an increase in the fibers' relative diameter with up to 35% could be observed, due to both structural modifications that occur in the cellulose macromolecular assembly and crystallinity and possible imidazolium cation grafting on the fibers, as suggested from the SEM micrographs, presented in Figure 2.16.

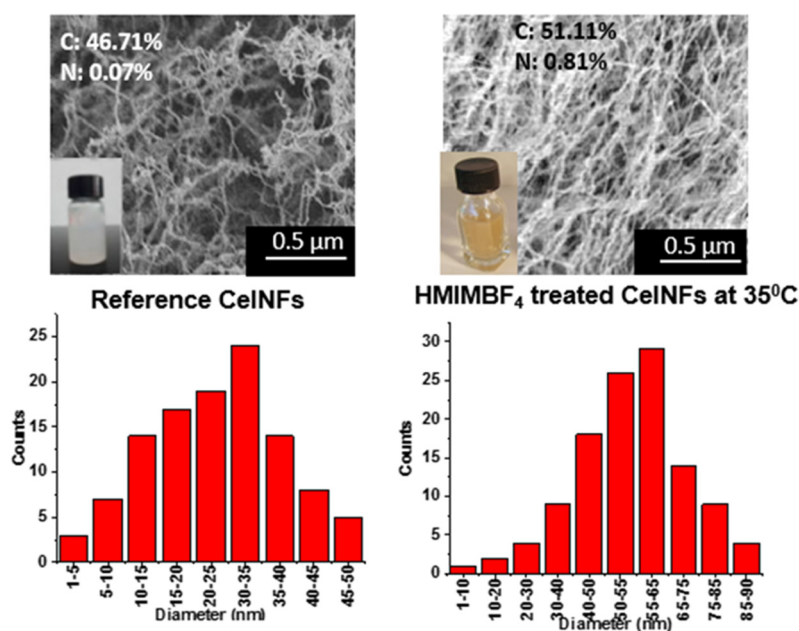


Figure 2.16. SEM micrographs, fiber diameter distribution and elemental (C, N) content of reference and IL-treated CeINFs (Croitoru and Patachia, 2016)

An elemental C and N percentage increase in the washed and irradiated-HMIMBF₄ treated CeINFs at 35°C may also suggest possible functionalization of cellulose with the partially hydroxylated imidazolium moiety, possibly by acetalization.

In *section 3.3* are discussed the application of these functionalized fibers to obtain polymer composite materials.

2.7. Ionic liquids as solvents and carriers for materials coating and impregnation

Application of organic coating has been among the oldest (namely oil-based or gelatine-based formulations) and most frequently used methods employed for cellulosic materials (wood) protection (Bulian and Greystone, 2009). In the latest years, growing interest has been shown in developing environmentally friendly wood coatings based on biopolymers, such as starch, chitin, or chitosan (Robinson et al., 2008). The advantages of using such polymers in wood impregnation are higher compatibility with polar adhesives and improved biodegradability at the end of the life cycle (Bulian and Greystone, 2009).

Studies demonstrated that the wood's highly polar surface has an excellent affinity to protein or cellulose derivate biopolymers (Brine et al., 1991).

Inorganic coatings have long been employed due to their excellent mechanical and thermal performance and higher bacterial resistance comparing to organic coatings (Kartal et al., 2007). Studies demonstrated that the highly polar surface of the wood, due to its hydroxyl groups, is well suited for grown or deposit of inorganic particles, such as silicon dioxide, titanium dioxide, sodium silicates, or hydrosoluble borates (Denes et al., 1999).

Biopolymers in coating wood or other related cellulosic materials pose some drawbacks due to such polymers' limited dissolution ability under "conventional" conditions. Also, inorganic compounds as particulate materials use in wood impregnation has been limited due to their low dispersibility and penetrability into the bulk of the wood.

I have researched a direction to use ionic liquids in wood coating and impregnation due to their high solvation ability for natural polymers or small-molecular natural resins, respectively, to their high dispersing ability for particulate inorganic materials. Due to the efficient swelling of wood by the ionic liquids, the mentioned compounds can diffuse into the wood. By water (or other non-solvent) addition, they precipitate into the wood's structure, leading to the formation of a continuous coating that confers dimensional stability and high hardness values.

The advantages of the proposed method of impregnation I have proposed are the usage of non-volatile and green solvents such as ionic liquids on the one hand, and lower temperatures (40°C) than conventional processes (100-200°C) on the other hand. The impregnation process's duration lies within 30 minutes, considerably lower than other traditional processes (Croitoru et al., 2016a; Patachia et al., 2016).

2.7.1. Impregnation with biopolymers and resins via ionic liquids

This subsection presents an innovative wood impregnation method with ecologic biopolymers and resins, such as chitosan (CHS), zein (ZE), gelatine (GEL), and guaiac resin (GR). The IL 1-ethyl-3-methylimidazolium chloride (EMIMCl) was used as a solvent. The impregnation method was patented in 2016 and could constitute a viable alternative to traditional methods of impregnation (Croitoru et al., 2016a). It applies to other types of alkylimidazolium ionic liquids and lateral alkyl chains from butyl to dodecyl. Norway spruce wood (*Picea abies L.*) has been used as a test material, but the method's suitability spans to other more difficult to coat and impregnate wood types (oak, beech, etc.).

The impregnation process comprises four steps, namely (1) - obtaining the chitosan, guaiac resin, gelatine and respectively zein solution in EMIMCl ionic liquid; (2) - impregnation of wood by immersion in the obtained dispersions at 40°C, following by (3) - the precipitation of the impregnating agent into the wood structure by water addition (IL removal) and finally (4) - drying the impregnated material (Croitoru et al., 2015a).

Several properties of the impregnation coating process (the wood percent gain, WPG) as well as of the impregnated material (Brinell hardness and surface energy $-\gamma$) are given in Table 2.3.

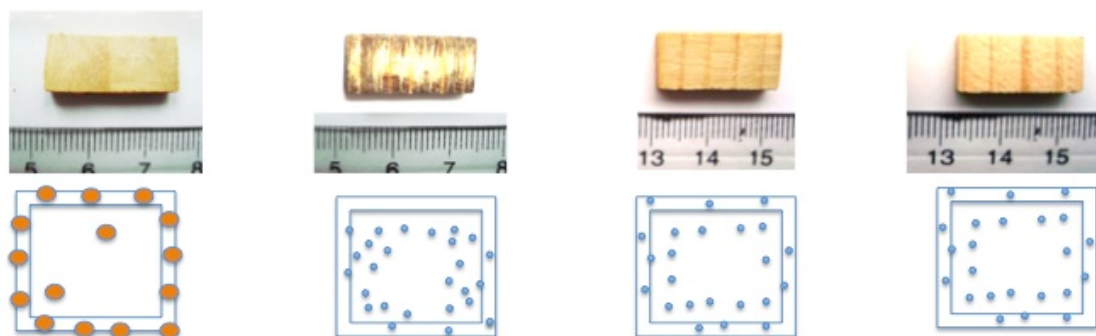
Table 2.3. Parameters related to the impregnation process and the properties of impregnated wood (Croitoru et al., 2015a)

Material	WPG (%)	Brinell hardness	γ (mN/m)
Wood (reference)	-	41.60	43.66
Guaiac resin-impregnated wood	15.11	68.63	39.86
Zein-impregnated wood	16.22	54.60	41.11
Gelatine-impregnated wood	19.26	58.57	42.48
Chitosan-impregnated wood	20.19	87.68	39.44

The WPG value represents the relative amount of impregnant, reported to the mass of oven-dried wood (expressed as percent value) that has been retained in the structure of the wood, after IL removal and drying of the material. The higher the WPG, the more efficient the impregnation process. Based on the volumes and concentrations of the impregnant solutions, the maximum WPG that can be attained with the proposed method is in the range of 15-20 %, considering that the ionic liquid is used only as a carrier and it is eliminated from the material in the precipitation step. For this reason, the WPG values from Table 2.3 are lower than those of other traditional processes (50–200%) (Liibert et al., 2011; Yuan et al., 2011) where all the absorbed impregnation dispersions (resins, monomers) are fixed into the wood's structure, contributing to the WPG.

It could be noted that generally, the thicker the coating of the impregnant on the surface of the wood, the higher the Brinell hardness. Chitosan, having the highest molecular weight from the studied impregnants could be more retained at the surface, while the other lower molecular weight impregnants are able to penetrate into the structure of the wood (Figure 2.17), generating lower values for the Brinell hardness than the chitosan-impregnated sample.

CHS impregnated sample GR impregnated sample ZE impregnated sample GEL impregnated sample

**Figure 2.17.** Scheme depicting the organic materials diffusion into the wood (Croitoru et al., 2015a)

The Brinell hardness tests have demonstrated that the wood impregnation increases wood hardness by up to 65% more than the non-impregnated reference. Also, by the method of impregnation I have developed, wood hardness can be improved to such an extent to resemble other exotic, expensive, or less accessible wood species, such as Jarrah (62 MPa) or Merbau (56 MPa) woods (Hill and Jones, 1999).

SEM analysis has been performed to evidence the wood morphology changes as result of the impregnation process that could explain the properties of the impregnated wood. Figure 2.18 presents the SEM cross-section images of impregnated samples and reference wood. For the reference wood, several structural features, such as tracheids displaced in parallel radial rows, bearing inside circular areolate pits could be observed.

It could be noted that the impregnated wood structure seems to be more consolidated due to tracheids shrinking. This could explain the higher Brinell hardness values obtained for impregnated wood, in comparison with the reference.

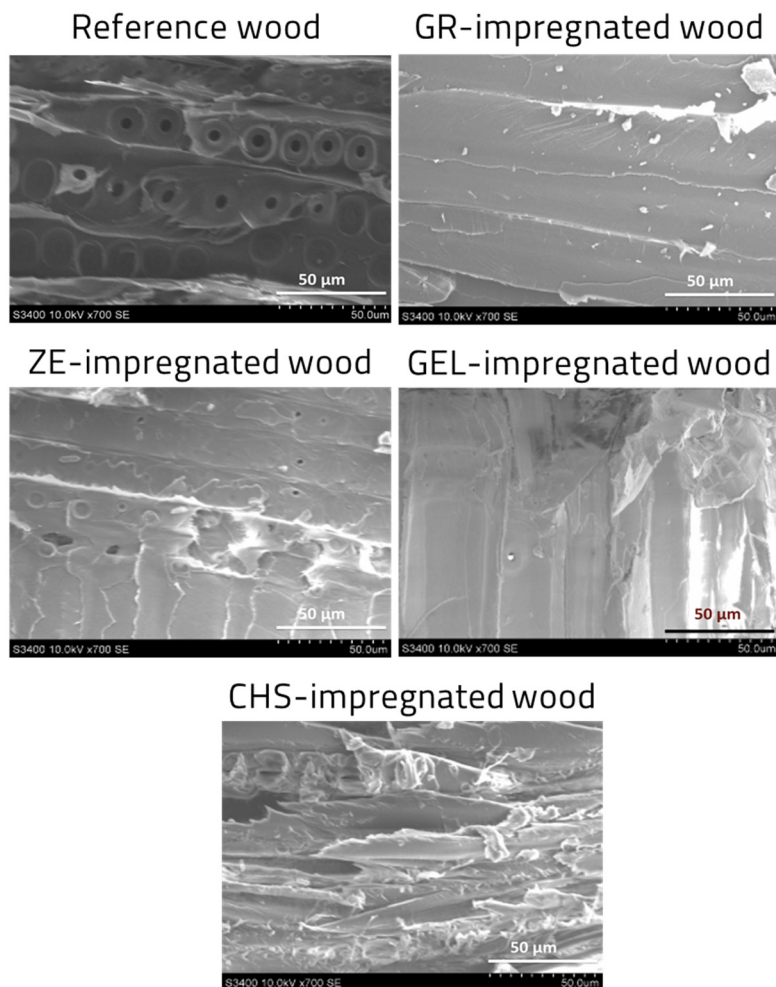


Figure 2.18. SEM micrographs of impregnated wood and reference wood (Croitoru et al., 2015a)

Also, even if the tracheid walls are still visible in the impregnated samples, the areolate pits inside them seem to be covered by the impregnant. The higher coverage degree of the areolate pits is registered by the guaiac resin and chitosan impregnated materials. Also, the proposed impregnation method does not significantly alter the wood's hydrophilic character, which ensures compatibility with polar adhesives or coatings.

2.7.2. Wood impregnation with inorganic compounds via ionic liquid carriers

The wood's polar surface is suited for the grown or deposit of inorganic particles, such as silicon dioxide, titanium dioxide, sodium silicates, or hydrosoluble borates (Kartal et al., 2007).

Some drawbacks regarding silicates and borates are the long period of impregnation (up to 24 hours), and the high hydrophilic character imparted to wood, which in some cases is undesirable. Up to this date, titanium dioxide has only been obtained in the wood's structure by the sol-gel process, starting from toxic and expensive organometallic precursors, such as tetrabutyl orthotitanate (Sun et al., 2010).

Alkylimidazolium halide ionic liquids can be applied as carriers for several nano- or microparticulate inorganic materials, aiding their penetration into the wood structure. The inorganic particles fill the pores and voids of wood, acting as moisture stabilizers. Also, due to their intrinsic properties (as ceramic powders), they can increase

the overall hardness of wood to match more expensive wood species. The impregnation method with inorganic particles comprises the same steps as those described in *subsection 2.51* (Patachia et al., 2016).

I have studied several inorganic particles' feasibility as impregnants for wood and ionic liquids with different lateral alkyl chains' dimensions. In this subsection, I will exemplify the results in conjunction with 1-ethyl-3-methylimidazolium chloride (EMIMCl) ionic liquid and several inorganic powders: TiO_2 (Degussa, with an average particle diameter of 21 nm); WO_3 (average particle diameter of 100 nm) and CaSiO_3 (average particle diameter of 74nm) (Croitoru et al., 2015b).

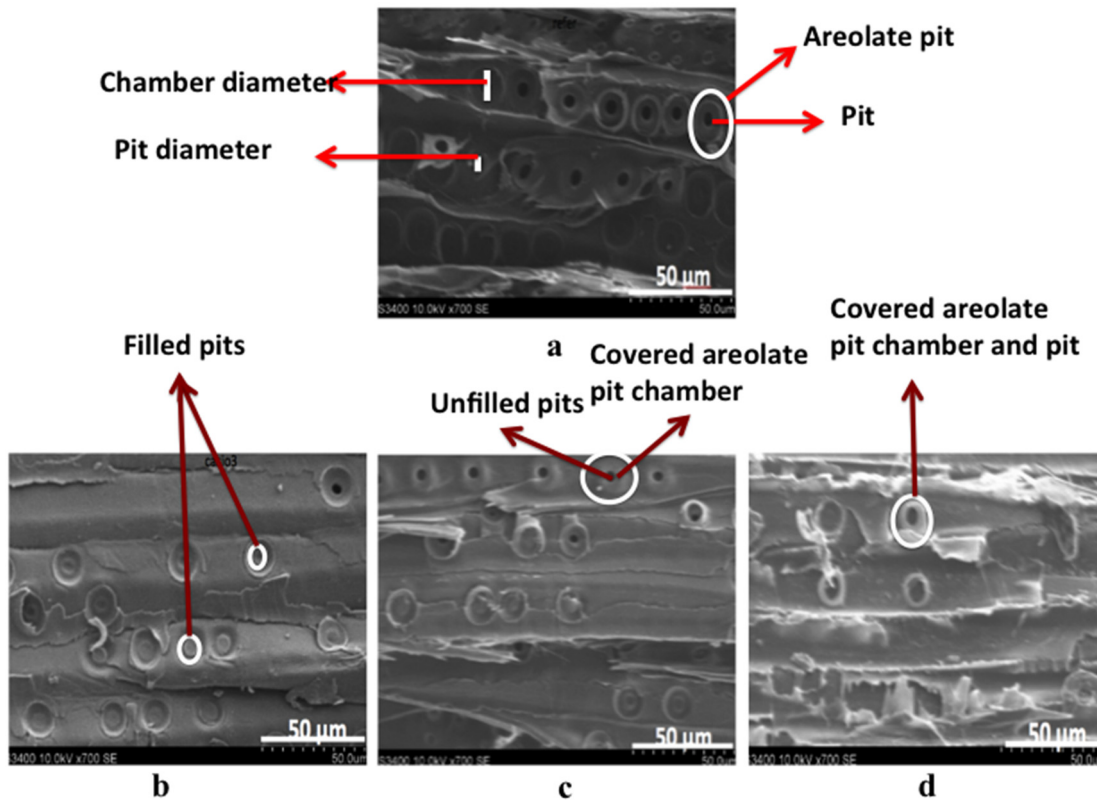


Figure 2.19. Cross-sections SEM micrographs of reference: non-impregnated wood (a) and impregnated wood (b) CaSiO_3 ; (c) TiO_2 ; (d) WO_3 at 50 μm scale (Croitoru et al., 2015b)

The impregnated wood structure seems to be more consolidated due to tracheids shrinking evidenced by the decrease of their diameter from 38.91 μm for the reference to 29.41 μm in case of the CaSiO_3 impregnated wood, to 27.96 μm for TiO_2 impregnated wood and to 27.97 μm in case of WO_3 impregnated wood (Figure 2.19). The tracheid wall thickness evidences a small increase in the case of TiO_2 impregnated wood (6.79 μm) and a higher increase in the case of CaSiO_3 impregnated wood (9.50 μm) and respectively of WO_3 impregnated wood (11.13 μm).

The smaller size of TiO_2 could explain the small increase of the tracheid wall thickness in TiO_2 impregnated wood by comparing with the other impregnants and due to the higher diffusion into the wood structure.

The shrinking of the impregnated wood structures could also be evidenced by the decrease of the areolate pit chamber diameter from 19.09 μm in case of the reference to 13.71 μm , 13.38 μm and 13.26 μm in case of CaSiO_3 ; TiO_2 and respectively WO_3 used as impregnants.

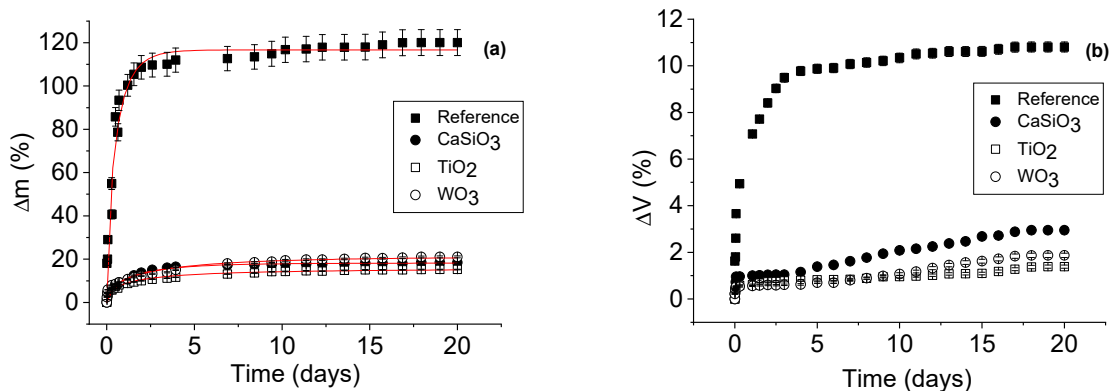
Also, as a function of particle diameter and interaction with the wood structure, the impregnant deposit could either be dominating obturate the pits (in case of CaSiO_3), or it can be dominating cast on the areolate pit chamber walls (in the case of TiO_2 and WO_3).

Several properties of the impregnation coating process (the wood percent gain, WPG) as well as of the impregnated material (Brinell hardness and surface energy $-\gamma-$) are given in Table 2.4.

Table 2.4. Parameters related to the impregnation process and the properties of impregnated wood (Croitoru et al., 2015b)

Material	WPG (%)	Brinell hardness	γ (mN/m)
Wood (reference)	-	41.60	43.66
TiO ₂ -impregnated wood	18.22	64.71	46.56
WO ₃ -impregnated wood	13.45	61.54	41.51
CaSiO ₃ -impregnated wood	14.90	66.82	63.15

In the impregnated samples, the inorganic particles that diffused into the pores of the wood act as a barrier for water absorption. In this case, sorption rates are lower than in the case of the reference. The pattern of water uptake suggests a possible two- step process, in which more than half of the final absorbed water occurred in the first two days of water contact with the wood. This is followed by a period of very slow but ongoing slight water uptake (Figure 2.20a). The time required for the material to reach the moisture content of about 63% of the total absorbed water at the end of the first phase of absorption is higher than that of the reference, demonstrating the beneficial effect that the inorganic impregnants have in retarding water sorption rate. CaSiO₃ particles may react with atmospheric moisture in order to form a uniform coating that could be able to retard the water sorption in the first step in a more efficient manner than TiO₂ or WO₃.

**Figure 2.20.** Water uptake kinetic curves (a) and dimensional volume modifications (b) of the impregnated samples and reference (Croitoru et al., 2015b)

Regarding the relative modification of the samples volumes, after 20 days of immersion in water (Figure 2.20b), it can be remarked that in the case of the impregnated samples minimal volume change has been registered (only 15-20% of the relative volume change of the reference). The lowest volumic change is attained for the TiO₂ impregnated sample, due to its ability to diffuse into the pores of the wood, avoiding cellulose swelling due to water penetration.

It is to be remarked that nano-size of the impregnant is important only in the diffusion process involving the swollen wood structure. In the collapsed structure, the nanoparticles agglomerated, filling the pores, and decreasing the permeability against water.

Wood impregnation increases the hardness of wood with up to 55% more than the non-impregnated reference. This demonstrates that the impregnation may come in useful when designing wear and scratch resistant materials, such as floor decks or for outdoor applications. The higher Brinell hardness values obtained in the case of CaSiO₃ impregnated sample could be due to the retention of silicate particles at the surface of the wood, due to their highest dimensions in comparison with the other used impregnants. Ca(OH)₂ formation at the surface

during the conditioning of the composites, which may slowly react with atmospheric CO_2 , forming CaCO_3 , may generally increase the resistance to deformation. TiO_2 and WO_3 particles, due to their lower dimensions, may penetrate the mass of the wood, contributing with a lesser amount to the overall surface hardness.

The main advantage of this novel and simple impregnation method is related to the ionic liquids' ability to swell wood, which accounts for better penetration of the impregnant into the bulk of the material. Wood swelling is difficult to attain in a short period by using conventional methods and solvents. Moreover, due to their null vapor pressure, alkylimidazolium ionic liquids do not contribute to atmospheric pollution, such as volatile organic compounds.

2.8. Ionic liquids as reconditioning agents for cellulosic artifact materials

One of the most important part of the cultural heritage of humanity is represented by paper artefacts, such as books, manuscripts, leaflets, sketches, drawings, photographs and so forth. Due to different support paper processing methods and artefact storage conditions, all paper-based artefacts are prone to degradation in time, thus having a limited shelf-life (Marin et al., 2015). Degradation of paper artefacts usually implies a modification in their overall appearance (yellowing, staining, foxing, dyes, inks, and pigments color alteration) as well as a reduction in mechanical properties (brittleness, tackiness). Inesthetic staining and foxing of paper occurs due to chromophore groups formation in cellulose, hemicelluloses, and lignin due to (bio)chemical degradation under the influence of light, humidity, temperature variations and atmospheric oxygen, or due to the sizers and binders (alum, rosin, gelatin and so forth) degradation (Marin et al., 2015). Reconditioning and conservation of degraded paper supports is a tedious multi-step task, implying eliminating the chromophore contaminants, consolidation of the material and applying protective agents (against environmental and/or biological factors).

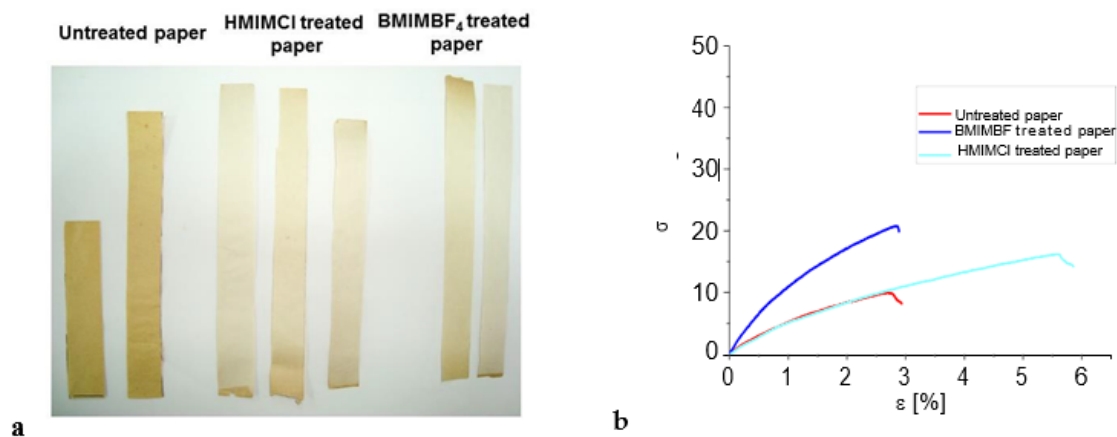


Figure 2.21. a: Photographic image; b: tensile test of reference paper and paper treated with ionic liquids BMIMBF₄: 1-butyl-3-methylimidazolium tetrafluoroborate; HMIMCl: 1-hexyl-3-methylimidazolium chloride (unpublished results, PN-III-P2-2.1-PED-2016 project proposal, 2016)

In this research theme, I have used ionic liquids as reconditioning and conservation agents for cellulose paper. Ionic liquids have high solvation ability for a large variety of organic and inorganic compounds, which may determine higher stains and foxing removal from the cellulosic material (Figure 2.21a). Washing the paper with ionic liquids determines a combined plasticizing (illustrated by the increase in the elongation at break with 3-95% by comparing to the reference) and a strengthening effect (illustrated by the increase in the tensile strength with 1-87% comparing to the reference (Figure 2.21b).

Chapter 3. Polymer matrix composite materials via ionic liquids

3.1. Polymer matrix composites revisited: synopsis and motivation

Polymer matrix composites (PMCs), especially those with thermoplastic polymer matrix, have gained increased interest due to their low cost, superior resistance to corrosion and fatigue, high specific strength, and stiffness compared to neat polymers or traditional ceramic and metallic materials (Croitoru et al., 2018a; Mahesh et al., 2021). These composites are commonplace in aerospace and automotive industries, trending to new domains such as the construction and biomedical fields. Additionally, PMCs offer greater design flexibility and superior resistance to corrosion and fatigue. The polymer composite's reinforcing agent can be obviously in any form (fibers, powder, flakes) and can be either inorganic, organic, or both types in more recent hybrid composite materials (Croitoru et al., 2018b).

Tuning the polymer-reinforcing agent assembly to good mechanical properties and improved outdoor use resistance is challenging. The addition of various compatibilizers (due to the distinct polarity of the matrix and filler) (Croitoru et al., 2017a), UV-stabilizers, fire retardants, fungicides, lubricants, and dispersing agents for the reinforcing phase (Ayrilmis, 2013) is needed to name a few. Most of these additives raise important environmental and health-related issues, some of the agents being widely recognized as potentially toxic and carcinogenic.

Due to their highly tunable polarity and affinity for a broad category of materials, ILs have already been used as compatibilizers for different biopolymer or synthetic polymer blends (Zeng et al., 2012), but not for composite materials.

A research direction with good application potential in the domain of composite materials was materialized in the framework of the *Young Research Teams* project entitled "Polyolefins and calcite wastes recycling by obtaining new composite materials" financed by UEFISCDI (PN-II-RU-TE2014-4-0173) for which I was project director and developed further in several research papers (Croitoru et al., 2016b; Croitoru and Patachia, 2016; Croitoru et al., 2017b; Croitoru et al., 2018a). It is related to ionic liquids' use as multipurpose additives for obtaining polymer composites with inorganic and organic filler materials.

Often, the chemistry of the additives required for a PCM material does not allow for their multipurpose use, e.g., a compatibilizer most often could not be used as a UV-stabilizer an antifungal agent simultaneously. Most often, many such additives are compounded in the material for its optimum attended use.

I have demonstrated that ionic liquids based on alkylimidazolium, alkylphosphonium, and alkylammonium cations improve the interfacial adhesion between organic (wood sawdust, cellulose fibers) or inorganic (marble, talcum) reinforcing agents and polyolefin matrices. In addition to the compatibilization effect, which directly influences the PCM materials' mechanical performance, the beneficial role of the ionic liquids has been extended to dimensional moisture stabilization and improving the composite's resistance to UV exposure.

Ionic liquid cation moieties have been grafted onto cellulose fibers by β (electron beam)-irradiation for improved compatibility with the thermoplastic polymer matrix (Croitoru and Patachia, 2016). While grafting different moieties to cellulose (through chemical means, plasma, or high energy radiation) has been successfully used since the early 1900s, ionic liquid cations grafting onto cellulose have not been previously successfully attempted.

I have also applied a new approach in obtaining wood composites based on sawdust dissolution and dispersion in alkylimidazolium ionic liquids following the removal of the ionic liquids by adding a non-solvent (water, ethanol). Entirely lignocellulosic composites were obtained, with precipitated lignocellulose acting as a binder for the undissolved wood sawdust particles. The composites are bear resemblances in concept to traditional agglomerated wood panels, but without using a synthetic thermosetting resin (Croitoru and Patachia, 2014).

I have assessed ionic liquids' usefulness as dispersing media for nanosized reinforcing fillers (carbon nanotubes) in polyolefin matrices and as means to obtain materials for hydrogen storage applications. These results will be summarized in the following subsections.

3.2. Wood-polymer composite materials with ionic liquid additives

The limited compatibility of the wood filler with the polymer matrix (usually thermoplastic polymers are used) leads to the obtaining of brittle and low-wear resistance composite materials, needing the addition of expensive (malleated polyolefins, copolymers of ethylene and vinyl acetate) and often toxic (siloxanes, isocyanates, chlorinated paraffins and so forth) compatibilizing agents. Malleated polyolefins are reported to increase the flexural and tensile moduli with only 1-10% at 0.5-3% loading amount, higher loading amounts presenting a detrimental effect on the mechanical properties. Secondly, susceptibility to fungal attack (white and brown rot, mildew) and weathering issues (moisture absorption, discoloration due to UV-exposure) limits the use of wood-polymer composites (WPCs) mainly in indoor media, needing further additivation with toxic biocides and UV-stabilizants, increasing the overall price of the product and hindering its recyclability (Klyosov, 2007).

A novel idea that I have developed and researched to mitigate the wood filler-polymer matrix compatibility issues was to use long-chain alkylimidazolium, alkylammonium, alkylphosphonium and alkylpyridinium room temperature ionic liquids as additives in WPC materials. These ionic liquids act as surfactants, having a high affinity for cellulose and lignin, as well as for the polymer (through the hydrophobic alkyl chains) (Figure 3.1).

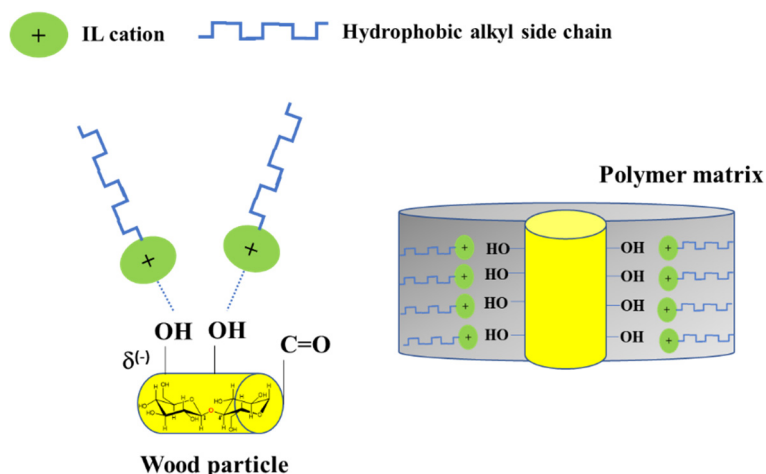


Figure 3.1. Principle scheme of ILs compatibilization effect in polymer matrix composites with wood filler

The ILs could be used simultaneously as compatibilizers between wood and the thermoplastic matrix, as plastifying agents, UV-stabilizants, thermal stabilizers, fire retardants and as fungicides, improving the properties of the materials and extending their lifecycle (Croitoru et al., 2017b; Croitoru et al., 2018a).

The wood-polymer composites (WPCs) containing ionic liquids I have obtained were obtained by compression molding (Croitoru et al., 2018a).

The filler of the composites consisted in oak (*Quercus robur L.*) wood sawdust with an average particle size of 220 μm . Two RTILs, namely methyltrioctylammonium bis (trifluoromethylsulfonyl)imide (MTOIm) (melting point of -55.43°C , boiling point of 484.1°C at 1 atm) and trihexyltetradecylphosphonium bis (2,4,4-trimethylpentyl) phosphinate (TTDPP) (melting point of -23.76°C , boiling point of 203.2°C at 1 atm) were added to the wood sawdust in a ratio of 0.1g/g dry wood. Two different wood filler loads have been used, namely 10% and 30%. The wood/wood+IL filler has been mixed with the polymer (HDPE) and compressed at 10 MPa at a molding temperature of 140°C .

The coding of the samples discussed in this section is as follows: HDPE-W10-MTOIm and HDPE-W30-MTOIm for the WPCs obtained with the MTOIm IL, at 10% and 30% wood loadings; and respectively, HDPE-W10-TDPP and HDPE-W30-TDPP for the WPCs obtained with the TDPP IL, at 10% and 30% wood loadings. The IL percentage for each composite is 1% wt. for the 10% wt. wood composites, respectively 3% wt. for the case of 30% wt. wood loading. The amounts of ionic liquids added are comparable to coupling agents or antifungal agents amounts reported for commercial additives (Williams, 2005). Reference samples, without IL in composition have been obtained following the same procedure and codified HDPE-W10, respectively HDPE-W30. Pure HDPE samples were obtained by pressing HDPE powder and molding at the same temperature as described above.

Morphology and structure of the WPCs

The scanning electron micrographs of impact fracture surface of the WPCs with 30% wood in composition, chosen as representative for the obtained composites are illustrated in Figure 3.2.

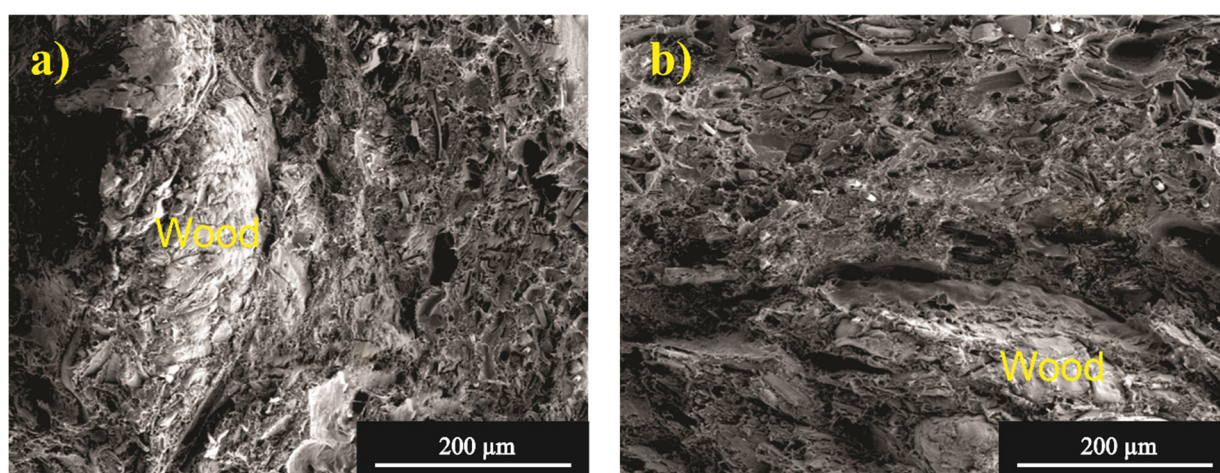


Figure 3.2. SEM micrographs of (a) HDPE-W30 and (b) HDPE-W30-MTOIm (Croitoru et al., 2018a)

The results of my research have indicated that in the case of the ionic liquid-containing composite (Figure 2.2b), the thermoplastic polymer matrix embeds the wood particles in a satisfactory manner, even if some local phase separation occurs. Some air inclusions (as porosity) could be also noted, being specific to the compression molding technique. The polymer matrix forms a mesh-like structure, indicating a dominantly plastic deformation mechanism (Li et al., 2003) with optimal mechanical properties, confirmed also by the results from Table 3.1. This behavior is similar also for the TDPP-containing composite.

The presence of IL in the composite, which interacts through physical bonding with the wood phase determines the improvement of interfacial adhesion between wood and the HDPE matrix, through lowering the surface energy of wood.

Through mapping the differences in the elastic force constant k of the silicon cantilever tip in semicontact mode AFM, further insights could be obtained from the phase distribution in the impact fractured surfaces of the obtained composites (Figure 3.3).

In phase imaging, lighter-colored areas present lower values for the force constant, i.e., the respective phase is harder and generates cantilever vibrations with reduced amplitude (Pandey et al., 2006). In contrast, "softer" phases allow for a higher amplitude vibration of the AFM cantilever tip. These phases usually appear as darker-colored.

The darker phases from Figure 3.2 possibly represent softer phases such as wood, IL-covered wood, or even IL-covered HDPE, while the lighter-colored areas could represent the neat-HDPE polymer phase. Ionic liquid migration/coverage into/of adjacent phases is consistent with other research, directed mainly on IL-containing polymer blends (Yousifi et al., 2014).

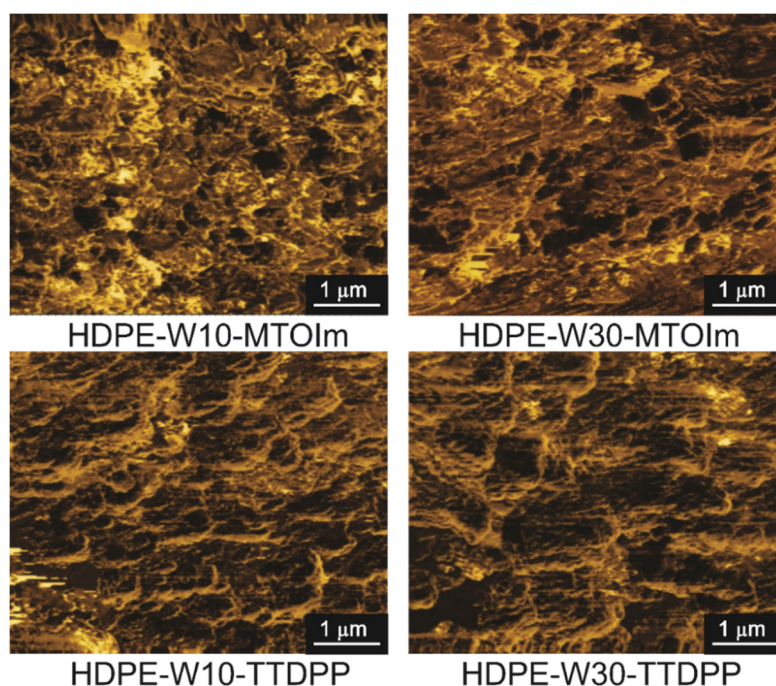


Figure 3.3. Phase imaging micrographs of IL-containing WPCs (Croitoru et al., 2018a)

The ATR-FTIR spectra performed on the obtained composites (Figure 3.4) confirm the presence of the ionic liquids on the surface of the wood sawdust, through the presence of different S-O vibration modes at $\sim 1344\text{ cm}^{-1}$ and $\sim 820\text{ cm}^{-1}$, imidic C-N at 1180 cm^{-1} for MTOIm (Suneetha et al., 2017) and respectively P=O vibration at $\sim 1170\text{ cm}^{-1}$ and P⁺-C stretching at 1335 cm^{-1} for TTDPP (Hernández Battez et al., 2016). The presence of these absorption bands of the IL on the surface of the material could imply a good compatibility with the thermoplastic matrix, and were marked with asterisk on the corresponding spectra from Figure 3.4.

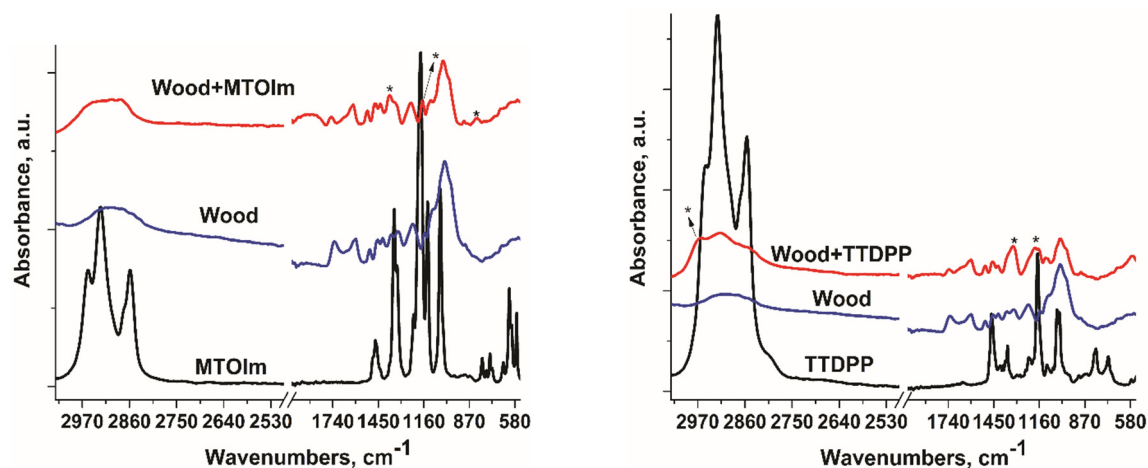


Figure 3.4. ATR-FTIR spectra of ILs, HDPE and IL-treated sawdust (Croitoru et al., 2018a)

As the ATR-FTIR spectra of the IL-containing composites and their components suggest (Figure 3.5a and 3.5b), the interaction between the wood-IL, respectively wood-polymer phase is of physical nature. No supplementary bands appear in the spectra of the composites, comparing to those of the pure components (wood, HDPE, IL).

Both in the case of MTOIm and TTDPP composites, ATR-FTIR spectra evidences good coverage of the wood phase with the polymer, the overall appearance of the spectra for the composites resembling that of HDPE (strong alkyl vibrations in the $2980\text{--}2870\text{ cm}^{-1}$ domain), also with several weak absorptions belonging to the ionic liquids marked with asterisk on the corresponding spectra from both Figure 3.4a and 3.4b, indicating possible migration of IL from wood to the HDPE phase.

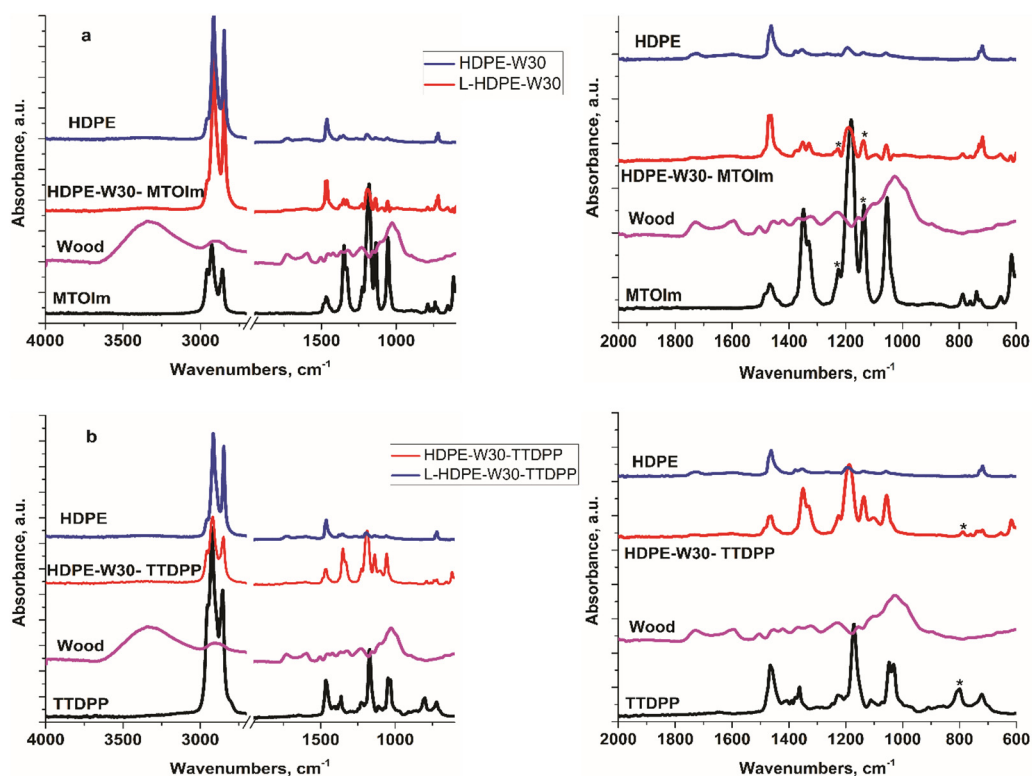


Figure 3.5. ATR-FTIR spectra of IL-containing WPCs: (a): with MTOIm and (b): with TTDPP (Croitoru et al., 2018a)

WPCs water stability and mechanical properties

Regarding the performance of the obtained composites, both in mechanical resistance as well as water stability, the results presented in Table 3.1 and Figure 3.6 respectively, show promising insights on future applications of this type of composites in humid outdoor applications (floors, decks, panels, and so forth).

Table 3.1. Water stability, wetting behavior and mechanical resistance of the WPCs (the standard deviation σ is shown in parenthesis) (Croitoru et al., 2018a)

Composite type	Δm (σ) (%)	ΔV (σ) (%)	K (σ) (kJ/m ²)	Wetting behavior			
				θ_{water} (°)	γ^{tot} (mN/m)	γ^{p} (mN/m)	γ^{d} (mN/m)
HDPE-W10	20.34 (3.11)	2.14 (0.29)	22.4 (2.37)	60.1 (1.21)	47.22	5.79	41.43
HDPE-W30	46.31 (3.78)	4.78 (0.61)	15.3 (1.92)	48.7 (1.32)	58.39	9.96	48.43
HDPE-W10 MTOIm	10.11 (1.72)	0.87 (0.08)	45.2 (2.01)	80.6 (1.05)	40.83	2.98	37.85
HDPE-W30 MTOIm	28.74 (2.63)	1.39 (0.12)	38.4 (3.12)	86.4 (1.43)	37.76	3.04	34.72
HDPE-W10 TTDPP	9.01 (1.32)	0.69 (0.07)	40.1 (1.78)	88.7 (1.78)	35.22	1.19	34.03
HDPE-W30 TTDPP	20.19 (2.05)	1.15 (0.15)	31.2 (2.04)	91.2 (1.84)	20.06	1.30	18.76

Evidently, HDPE being the majoritarian component, the mechanical properties of the obtained WPCs are dictated by this polymer and by the interfacial adhesion between wood and HDPE. Due to the improved interfacial adhesion between the wood and the polymer phases promoted by the ILs, an increased overall water stability of the IL-containing WPCs, with up to 60% both in terms of water uptake (Δm) and dimensional volumic stability (ΔV) could be noted from the results presented in Table 3.1, in comparison with the reference WPCs. Synergic with the improved interfacial adhesion between the components, the presence of the hydrophobic ionic liquids could act as a supplementary barrier for water penetration into the structure of the material. The importance of this synergic mechanism is sustained by the fact that the TTDPP ionic liquid can promote higher dimensional stabilization for the WPCs in comparison with MTOIm, probably due to its more pronounced hydrophobic character.

The improved interfacial adhesion between the wood and HDPE components could be also depicted from the values of the impact resistance (K). As delamination could occur in the reference WPCs submitted to mechanical stresses, owing to the poor interaction between the component phases, their impact resistance decreases with filler content increase. The presence of ionic liquids in the structure of the material doubles the impact resistance of the IL-WPCs, in comparison with the reference WPCs, for the same wood filler loading amount. In the case of impact resistance, interfacial adhesion plays a crucial role, so the highest performance is registered in the case of MTOIm-containing composites.

The hydrophobic character of both ILs and polymer matrix is imparted to the overall composite assembly, illustrated by the predominantly dispersive nature (γ^d) of the surface energy (γ^{tot}) (van der Waals interactions between components). The highest contact angle (θ^{water}) values, indicating a hydrophobic surface, even at 30% wood loading is achieved in the case of the composites containing the TTDPP ionic liquid, for which the water stabilization effect was also the highest. The low values of the polar component of the surface energy (γ^p) indicate a material with poor affinity to water and other polar solvents and may also be a potential indicator of a surface with anti-dust or anti-dirt adhering potential, contributing to the obtaining of materials with an increased life cycle. Also, a low value of the surface energy could impede also fungal hyphae adhesion or bacterial biofilm formation on the surface of the WPCs (Ista et al., 2004), contributing to the obtaining of materials with bactericide/bacteriostatic and/or fungicidal action.

The tensile behavior of the obtained WPCs (Figure 3.6) could be discussed also in terms of interfacial adhesion between the HDPE/wood components. Due to the specific nature of the filler and due to its interaction with the IL molecules, tensile behavior (with emphasis on the ultimate strain value) could be expressed also in terms of IL plasticization effect on cellulose, the main component of wood.

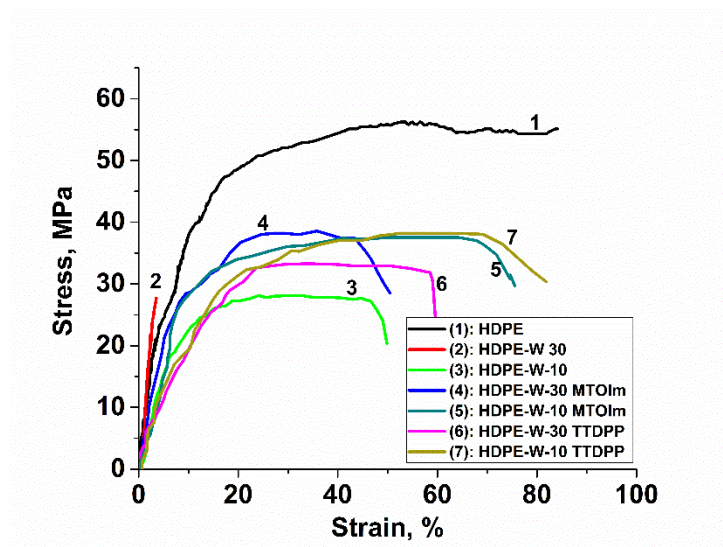


Figure 3.6. Stress-strain diagrams for WPCs and neat HDPE (Croitoru et al., 2018a)

The lower interfacial adhesion between wood and HDPE is responsible for an almost brittle-like behavior of the HDPE composite bearing 30% wood filler, without IL in composition. Comparing with neat HDPE, their tensile strength is twofold lower and their ultimate strain value decreases inversely proportional with the wood filler content. ILs generally act as hydrogen bonds disruptors for cellulose, increasing the flexibility and the relative movement of the macromolecular chains. As the cellulose-majoritarian wood matrix is being “softened” by the ionic liquid, the rigid architecture of the filler beads can be expanded, conducting to a remarkable increase in the strain resistance, comparable to that of neat HDPE, in the case of TTDPP, with the highest plastifying ability, at up to 40% lower tensile strengths. Even so, at ultimate tensile stresses ranging from 28 to 37 MPa, the obtained values are comparable with those from the reference literature, for similar wood loadings, respectively 15–28 MPa for WPCs with maleated polyethylene as compatibilizer, or 28–60 MPa for phthalic or succinic anhydride-modified wood usage (Hill, 2006; Lai et al., 2006).

Comparing with the use of chemically modified wood, blending of ILs into the composite material presents potentially higher economic efficiency, eliminating the need for tedious reaction preparation and washing steps, or the use of highly volatile organic solvents, with potential health hazard-related issues. In terms of compatibilizing agent specific consumption, in contrast to the frequently used maleated polyethylene or polypropylene compatibilizers, IL loadings could be as low as 1% reported to the filler, in contrast with 5–10% in the first case, which could mitigate production costs related to the higher price of the ionic liquids.

Accelerated light exposure resistance of the WPCs

The obtained IL-containing WPCs present an improved resistance to 150 h accelerated light exposure tests (UV-A), as demonstrated by the ATR-FTIR spectroscopy studies, owing to the stabilizing effect of the ILs. For these composites, this stabilization effect has been proven solely on FTIR spectroscopy (Figure 3.7), as the dark-brown color of the composites masked the overall color modifications. The irradiated samples are coded with “L” in front of the respective WPC code.

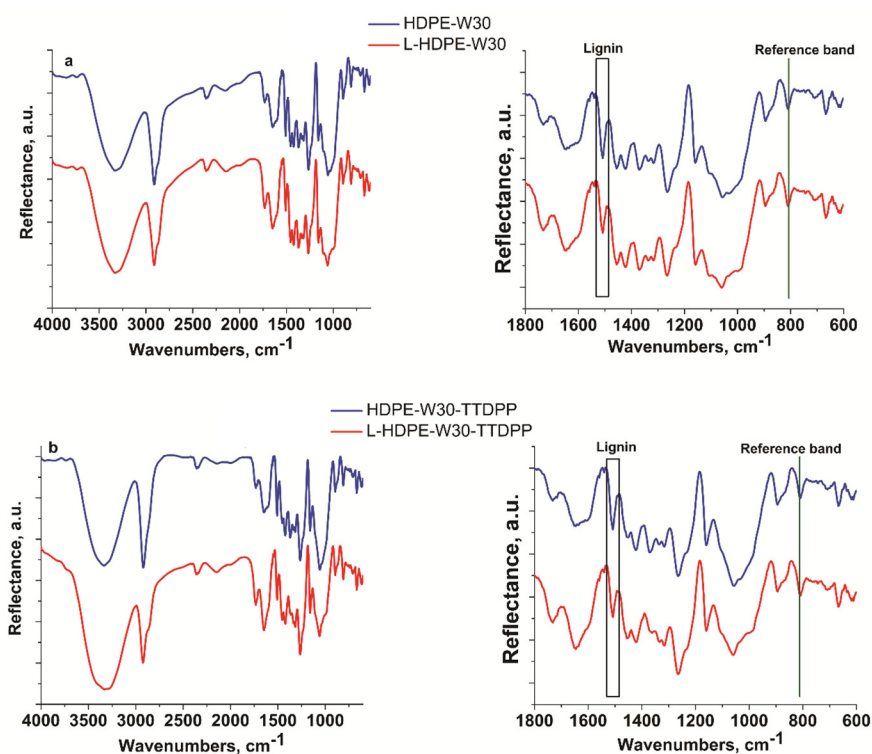


Figure 3.7. ATR-FTIR spectra of neat and irradiated a) HDPE-W30 reference samples; b) HDPE-W30-TTDPP samples (L: light irradiation) (Croitoru et al., 2018a)

The discussion regarding possible structural modifications which occur in the composites submitted to accelerated light irradiation testing has been further emphasized on the composites with 30% wood filler content (for which the most intense structural modifications occurred), for both reference and respectively the TTDPP-containing WPCs. The most promising photostabilization effect has been achieved in the case of TTDPP ionic liquid (Figure 3.7). Similar discussions could be conducted on MTOIm ionic liquid-containing composites. An interesting feature could be deduced through the comparison of the absorbance ATR-FTIR spectra of the samples (Figure 3.5) with those obtained by means of the integrating sphere (Figure 3.7). The larger surface scan area in the case of the spectra from Figure 3.7 (samples surface) evidences a more pronounced spectral contribution of the wood phase, probably due to the insufficient coverage of wood with HDPE near the molding matrix walls. Also, no distinct IR absorptions from the ILs have been detected (amounts below the detection limits of the method), probably due to its predominance in the bulk of the material, but the materials present distinct behavior to light exposure, proving its role possibly in free radical and oxidation inhibition. All the band intensity modifications have been reported to the intensity of the absorption centered at $\sim 812\text{ cm}^{-1}$, which was proven the most stable to oxidation in this case.

Accelerated 150 h photoinduced ageing of the reference WPCs leads to the formation of -OH groups, through the relative increase in the band centered at 3370 cm^{-1} (from alcohols, or carboxyl acids or peroxidic -OOH) in comparison with the non-irradiated reference. These groups could be formed either due to lignin and cellulose macromolecular chain scission and hydroxylation in the presence of moisture and atmospheric oxygen or due to polyethylene macromolecules oxidation, through Norrish II mechanisms (Fabiya et al., 2008). Also, carbonyl groups are formed, either from HDPE through Norrish I mechanism or from cellulose/lignin chain scission and oxidation (Abidi et al., 2017). The increase in the relative band intensity at 1732 cm^{-1} (ascribed to non-conjugated -C=O groups) after light exposure is 21.1% for the reference HDPE-W30 samples, while for the HDPE-W30-TTDPP samples it is only 13.54%.

The increase of the WPC hydrophilicity is also sustained through the relative increase of the broad band shoulder at 1635 cm^{-1} and $\sim 2100\text{ cm}^{-1}$ associated to weakly bonded water libration. For the L-HDPE-W30-TTDPP composite, a 35% lower decrease in the lignin characteristic band (1513 cm^{-1}) intensity occurs after accelerated photooxidation testing, in comparison with the reference sample.

The beneficial effect of ILs is not limited only to alkylphosphonium or alkylsulphonium ionic liquids, but also with long-chain alkylimidazolium ionic liquids.

In another study, the same method (compression molding) was applied to obtain WPC materials starting from Norway spruce (*Picea sp.*) wood sawdust and PP was used as matrix. The 1-dodecyl-3-metilimidazolium chloride ionic liquid was used and the loading amount of the reinforcing filler reported to the thermoplastic matrix was 10%, respectively 20% wt. The two types of composites are coded with WF10PP, respectively WF20PP (Croitoru et al., 2016c).

Table 3.2. Water stability and tensile properties of the WPCs (Croitoru et al., 2016c)

Composite type	Water absorption	Tensile properties	
	Δm (%)	σ_{break} (MPa)	E (MPa)
PP	0.98	70.23	367
WF10PP	2.34	50.45	404.23
WF20PP	3.32	46.54	411.16

Due to the hydrophilic nature of wood, the overall water absorption values of the PP matrix WPC materials (Table 3.2) are with 90-98% higher than those corresponding to neat polypropylene, but are comparable to the water

uptake values for other similar composites presented in the reference literature for the same wood loading amounts (maleic anhydride grafted polypropylene, polypropylene and acetylated wood, etc.)

The tensile strength of pure PP is decreased by at least 15-25% when wood flour was added. The tensile strength of composites is mainly influenced by filler fraction and the interfacial adhesion between particles and matrix (Sun et al., 2006). A satisfactory overall interfacial adhesion is responsible for the obtained mechanical data, in agreement with the values presented in the reference literature. Better adhesion between the ionic liquid treated wood results in more restriction to deformation capacity of the matrix in the elastic zone and increased modulus. Similar observations were reported for other lignocellulosic fibres-based PP composites (Ashori and Nourbakhsh, 2011).

The results of this research direction have shown that the ionic liquid additives do not modify the natural color of the wood filler and impart good impact and tensile resistance to the obtained material, such as those of several commercial wood-polymer composites. Also, the ionic liquids can improve the interfacial adhesion between wood and thermoplastic polymers while also providing stability to various weathering environments (presence of moisture or UV radiation).

3.3. Fiber-reinforced polymer composite materials with ionic liquid additives

Natural cellulosic fibers of wooden or non-wooden origin as well as highly crystalline cellulose-derived products (cellulose nanofibers) could be used as relatively inexpensive reinforcing agents in a large variety of thermoplastic (PE, PP) or thermoset resin (epoxy, phenol-based) polymeric matrix composites (Oksman et al., 2016). These fillers present a large variety of applications in the construction and automotive industry, due to their bioavailability, low machine wear in processing, low density compared to traditional inorganic fillers, low price, coupled with high impact resistance.

Cellulose nanofibers could be produced from a wide variety of sources; such as paper, wood pulp, natural cellulose fibers, through time and temperature controlled enzymatic or acid hydrolysis, selectively hydrolyzing only the amorphous part of the macromolecular cellulose chains (Kim et al., 2009).

However, due to the hydrophilic nature of cellulose, most of the obtained composites bear a cellulose-compatible polar polymeric matrix. To use CelNFs as fillers in polyolefin matrix composites, their surface must be modified either through physical (e.g., plasma grafting of fluorine or silicon atoms on the nanocellulose fibril surface) or chemical functionalization (esterification or coupling agent treatment), otherwise poor mechanical properties and delamination could occur (Espino-Pérez et al., 2014).

A newly-developed research direction I have developed resides in cellulose nanofibers functionalization through low temperature (25-35 °C) surface modification with long-chain imidazolium ionic liquid moieties, as described in section 2.4. To demonstrate the usefulness of the functionalization method for composite materials, I have used the functionalized nanofibers to obtain composites with HDPE matrix.

Different fiber to matrix loadings was tried, out of which two types of CelNFs-HDPE composites were found more representative and are discussed in this section. The composites were obtained through compression molding by using a 10% wt. weight ratio of CelNFs reported to HDPE: (1) reference samples, with neat cellulose nanofibers and (2) samples with irradiated IL-treated CelNFs at both 25 °C and 35 °C.

The HDPE thermoplastic polymer (in powder form) and the CelNFs have been pre-mixed and pressed at 5 MPa and then maintained at 230 °C for 1h, followed by cooling at room temperature.

The SEM micrographs from Figure 3.8 suggest an improved adherence of the cellulose nanofibers with the HDPE matrix. Even if cellulose nanofibril associations may occur, the analysis of the IL-treated CelNFs at 35 °C

composite does not evidence debonding or delamination, such as in the case of neat CeINFs-HDPE composite, where visible structural defects (voids, delamination) are present.

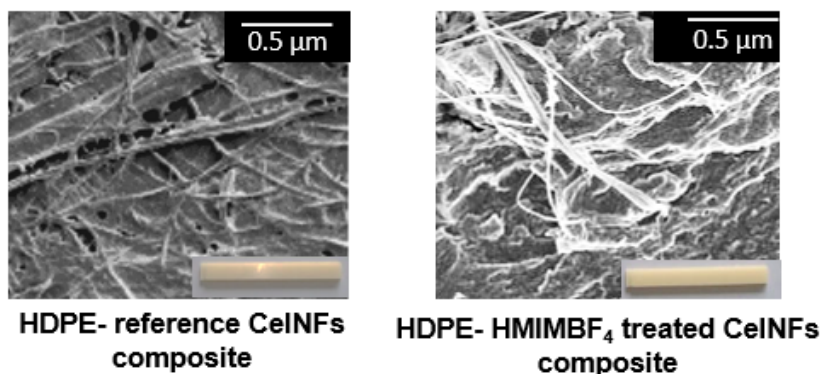


Figure 3.8. SEM micrographs of CeINFs-HDPE composites (Croitoru and Patachia, 2016)

The functionalization of the cellulose with the irradiated alkylimidazolium ionic liquid determines an improved adhesion of the nanofibers with non-polar matrices (polyolefins), thus constituting a possible alternative to other physical and chemical cellulose methods. Due to the low temperatures of functionalization (basically more or less around room temperature), it bears minimal intrusively regarding the bulk chemistry of cellulose and of the polymeric matrix.

3.4. Polymer-inorganic filler composite materials with ionic liquid additives

Inorganic materials represent a frequently employed category of fillers used to produce thermoplastic matrix composites, especially polyolefin-based (polyethylene and polypropylene). The addition of inorganic fillers in the polyolefin (PO) matrix leads, in principle, to a diminishing of the final cost of the material and to the improvement of its mechanical properties (rigidity, hardness, impact resistance and flexural resistance). Among the most frequently used inorganic fillers is amorphous calcium carbonate (60% of the total amount of inorganic fillers) (Leong et al., 2004; Özen et al., 2015).

One research thematic I have developed resides in utilizing crystalline inorganic fillers for composite materials with thermoplastic polyolefin matrix. Crystalline fillers have been used on a lower extent in obtaining composites with polyolefin matrix in comparison with amorphous ones (e.g., amorphous calcium carbonate). In this research domain I aimed to optimize the obtaining process of the composite materials with crystalline inorganic fillers, by establishing the influence of different parameters on the properties of the final composite.

Using crystalline inorganic fillers poses some difficulties arising from the limited compatibility of the crystalline filler with the thermoplastic polymer matrix and its tendency to agglomerate leading to the obtaining of low mechanically-resistant composite materials (Ahmed et al., 2013; Croitoru et al., 2016; Deshmane et al., 2007). The filler particles are ground at a diameter smaller than 5 μ m and are surface treated with surfactants to improve their dispersibility and compatibility with the thermoplastic polymeric matrix. Traditionally, stearic acid, calcium stearates, fluoro-alkoxysilanes are added in a weight ratio of 5%, reported to the filler (Tang et al., 2014; Li et al., 2009).

I have proposed using ionic liquids, compatible with inorganic fillers, as compatibilizers and dispersing agents for polyolefin-crystalline fillers composites. This was the theme of the research project PN-II-RU-TE-2014-4-0173, for which I was project director, spanning between 2015 and 2017.

Surface treatment of crystalline calcium carbonate with ionic liquids

Calcium carbonate is the most widely used filler for particulate-reinforced polyolefin composites, due to its low price, coupled with good thermal stability, workability, and neutral color. It has been reported to efficiently increase the impact resistance, fire-resistance, and water stability in various combinations with HDPE and PP matrices. However, due to its high surface polarity and hydrophilicity it is mainly incompatible with hydrophobic polymer matrices such as polyolefins (Croitoru et al., 2014; Croitoru et al., 2017b; Osman and Suter, 2002). To improve its dispersibility in polymer media, calcium carbonate is often surface treated with a variety of modifiers/dispersion agents such as silanes, phosphates, titanates, fatty acids (mainly stearic acid), etc. Because of this treatment, a layer of hydrophobic organic molecules is attached to the mineral surface, via physical bonding. The structure and properties of such layers, being the interface between the inorganic filler and the polymer matrix bears a strong influence on the final properties of the composites (Croitoru et al., 2016).

I have performed surface treatment experiments of crystalline fillers (marble, talcum) with various types of long-chain alkylimidazolium, alkylsulfonium and alkylphosphonium ionic liquids solutions in ethanol (Figure 3.9a and b). Herein is exemplified the methodology for the surface treating of marble powder with triethylsulfonium-bis(trifluoromethylsulfonyl) imide (TesIm) ionic liquid by treatment of the particles with different amounts of this ionic liquid dissolved in ethanol. The marble powder (sieved, average particle diameter < 0.01mm) was immersed in three solutions with concentrations of 30%, 50% and 50% vol. TesIm in 98% ethanol. The effect of surface modification has been evaluated by a simple flotation test. The test determines the ratio of the free-floating IL-covered powder to the overall weight of the powder after being magnetically stirred in water at 1000 rpm and room temperature (the so-called active ratio) (Croitoru et al., 2017b).

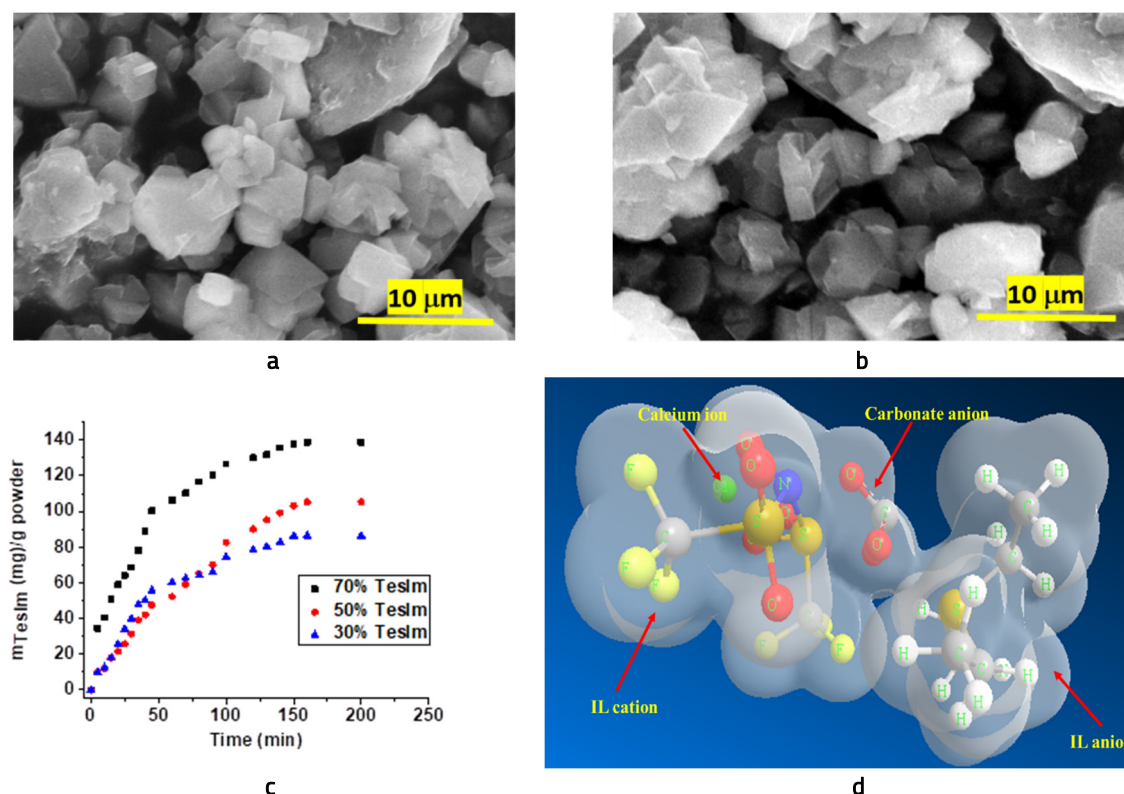


Figure 3.9. (a): SEM image of the initial marble powder and (b): SEM image of the powder treated with TesIm IL; (c): TesIm IL sorption kinetic onto the marble powder; (d): schematic depiction of the carbonate interactions with TesIm; (collated from Croitoru et al., 2017b)

The marble powder IL uptake kinetic presented in Figure 3.9c indicates that an equilibrium uptake of IL is reached in a relatively short time (approx. 150 min of contact with the IL ethanol solution). The maximum loading amount

of ionic liquid is registered for the solution with the highest IL content (70% vol.). The active ratio of the functionalized powder is 32.45 % for the marble immersed in the 30% vol. TesIm ethanol solution; 57.23% for the marble immersed in the 50% vol. TesIm ethanol solution and 65.23% for the 70% vol. solution, respectively.

It is expected that the calcium and carbonate ions in the marble filler interact with the anion/cation of the ionic liquid. Molecular dynamics simulations (MMF94 interface, 5000 iterations, minimum RMS gradient of 0.1) have indicated that calcium carbonate molecule is placed within the "solvation surface" of the ionic liquid. The Ca^{2+} anion surface charge is efficiently "masked" by the $-\text{CF}_3$ groups of the bis(trifluoromethylsulfonyl) imide anion (effective charge of +0.041) while CO_3^{2-} anion is attracted by charge-dipole interactions by the S^+ atom in the ionic liquid cation (effective charge of the two O⁻ ions being -0.64 and -0.71) (Figure 2.9d) (Croitoru et al., 2017b).

The marble powder presents a dominantly crystalline structure, as determined from the XRD diffractogram (Figure 3.10a). The as-received marble powder comprises mainly of trigonal calcite, rhombohedral dolomite, and several aluminosilicate minerals, such as aegirine, hypersthene, diopside, alongside quartz.

Ionic liquid adsorption on the surface of the marble particles determines a decrease in the overall intensity of the spectrum, probably due to the coating of the crystalline phases with the amorphous ionic liquid.

This hypothesis could be confirmed by the presence of the amorphous peak, centered at $\sim 19.7^\circ$ (Figure 3.10b). Also, several peaks, ascribed to hypersthene, diopside and dolomite disappear from the diffractogram, indicating that these inorganic compounds are being leached into the IL solution.

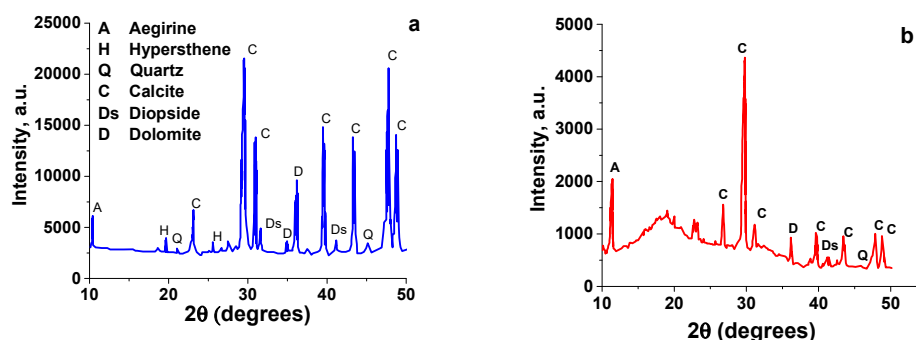


Figure 3.10. XRD diffractograms of: (a): neat marble powder; (b): TesIm-treated marble powder (70% vol. IL solution) (Croitoru et al., 2017b)

As the calcite phase has the higher hardness among the minerals present in marble, leaching of compounds with lower mechanical resistance could prove useful for the hardness and impact resistance of particulate-reinforced polyolefin composites.

The values presented in Table 3.3 for the IL-treated marble filler (70% vol. initial IL solution concentration) indicates a decrease with up to 54% in the values of the surface energy comparing with the untreated marble powder (for the measurements, the filler and the polymer powder were pelletized through applying identical pressures).

Table 3.3. Surface energy values of the analysed samples (Croitoru et al., 2017b)

Sample	γ (mN/mm)	Water contact angle ($^\circ$)
Marble	75.4	23.5
TesIm-treated marble	34.1	68.7
PP	30.4	56.1
HDPE	29.9	50.9

The values for the surface energy of the functionalized marble resemble those of PP and HDPE, indicating a good potential compatibilization between the two phases, beneficial to the obtaining of composites.

Polymer composites with ionic liquid-treated marble as filler

The IL-treated marble filler (reaching adsorption equilibrium in IL solutions and dried) were mixed with polyolefin (HDPE or PP) powders in various ratios and them compression-moulded at 50 MPa and 150°C (HDPE), respectively 180°C (PP) (these temperatures were chosen based on prior-made DSC analysis).

Concerning marble as crystalline filler, from the multitude of tested ionic liquids, triethylsulfonium-bis(trifluoromethylsulfonyl) imide (Teslm) has been found to convey the best tensile strength for the composites with PP matrix, while 1-dodecyl-3-methylimidazolium hexafluorophosphate (DMIMPF₆) was found beneficial for composites with HDPE matrix (Figure 3.11).

The optimal loading of the polymer matrix with this type of crystalline filler was found between 1-10% wt., values for which the tensile strength does not decrease to a significant amount.

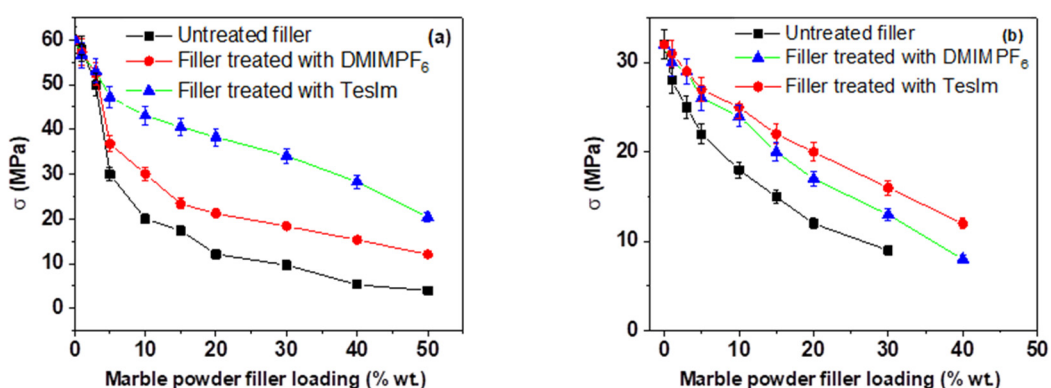


Figure 3.11. Tensile strength of the polyolefin matri composites additivated with ILs as a function of filler amount: (a): PP matrix; (b): HDPE matrix (unpublished results, [PNII-RU-TE-2014-4-0173 final synthetic report, 2017](#))

The marble powder filler is well embedded in the polymer matrix, probably due to the uniform asorption of the ILs on the surface of the inorganic particles. The ILs decrease the inorganic filler- organic thermoplastic polymer interfacial surface tension due to their hydrophobic nature. No cracks or pores are observed on the surface of obtained composites (Figure 3.12).

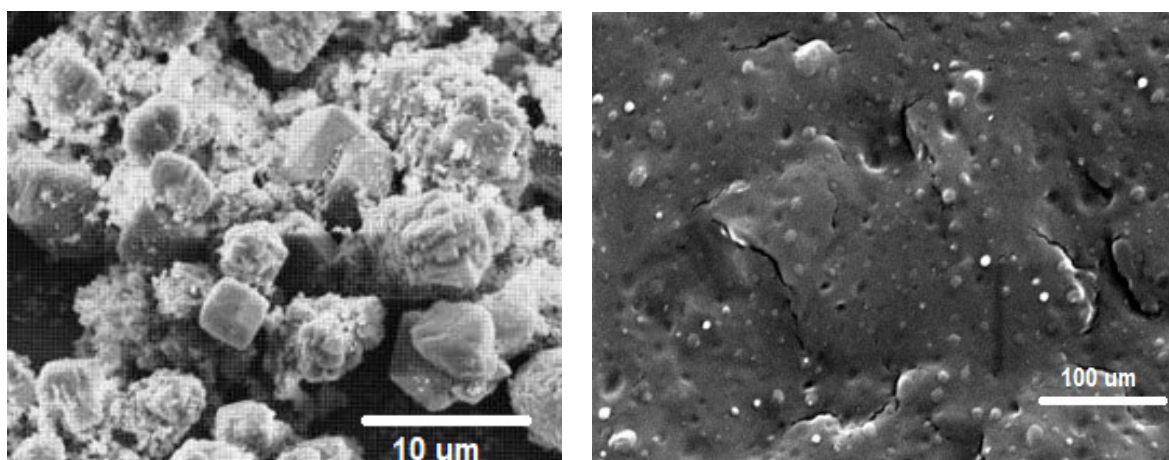


Figure 3.12. SEM micrographs of: marble powder treated with the Teslm IL (left); PP matrix composite with Teslm-treated marble filler (right) (unpublished results, [PNII-RU-TE-2014-4-0173 project final synthetic report, 2017](#))

The present research theme is important by the fact that it will conduct to a better capitalization of a non-biodegradable waste resulting from the construction industry (crystalline powders such as marble) and by the fact that it opens the possibility to utilize waste polyolefins as matrices, by embedding them in products with a higher-use value.

3.5. Biocomposite materials obtained with ionic liquids

Another direction of research that I have developed pertains to the obtaining of wood biocomposites by recovery of wood sawdust. The principle of this idea is to add wood sawdust in ionic liquids in an amount which surpasses its solubility limit, followed by precipitation by water addition. The cellulose and lignin precipitated from the corresponding ionic liquid solutions act as a binder for the undissolved wood particles, thus eliminating the use of non-ecological adhesives, such as formaldehyde-based resins (Croitoru and Patachia, 2014).

Biocomposite materials obtaining

I have obtained the wood composite materials by incorporating fir (*Abies sp.*) sawdust in three types of ionic liquids: 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-ethyl-3-methylimidazolium chloride (EMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl) at 100°C in a weight percentage of 20% reported to the ionic liquid. The values for the solubility limits of fir wood sawdust in the three ionic liquids at 100°C are: 7% wt. (in BMIMCl), 7.8% wt. (in EMIMCl), and respectively 9.8% wt. (in AMIMCl) at 100°C.

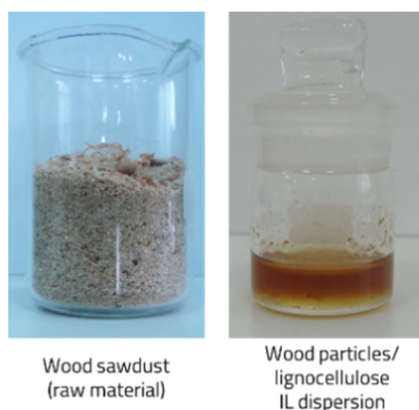


Figure 3.13. Photographic images of the raw wood material and of the wood/lignocellulose IL dispersion (POSDRU/89/1.5/S/59323 postdoctoral experimental report, 2012)

Since the solubility limit of the wood sawdust is lower than the added amount, only a part of the wood particles is dissolved in the IL, resulting a dispersion of wood particles into a lignocellulosic ionic liquid solution (Figure 3.13). The dispersion has been cooled to room temperature and compression moulded. The compression-moulded wood/ionic liquid mixture has been immersed in distilled water at room temperature to precipitate the lignocellulose by ILs removal (water is a non-solvent for cellulose and lignin). The final step in obtaining the “all wood” composites is represented by drying. The composites obtained with the three ionic liquids were coded with C-BMIMCl, C-EMIMCl and C-AMIMCl.

Biocomposite materials characterization

The presence of undissolved sawdust in the obtaining recipe leads to rough surfaces of the composites (Figure 3.14). The lower average roughness (R_a) for the composites compared to the reference (pressed fir sawdust),

indicates that the undissolved partially swollen sawdust particles are embedded in precipitated lignocellulose, leading to a smoother surface. Also, the surface roughness of the composites seems to depend on the lignocellulose dissolution ability of the ionic liquid. AMIMCI ionic liquid, which presents the highest lignocellulose dissolution ability, generates more dense composites with a smoother surface comparing to the BMIMCI ionic liquid.

Water sorption is a key parameter in determining the application domain of the wood composites. The water uptake of the composites stored in a medium of 86% relative humidity is 20% lower than the corresponding values for wood (Figure 3.15). The reference (pressed sawdust) is not water-resistant, as it disaggregates within the first minute of immersion. The water uptake values of the composites are comparable to those corresponding to untreated conditioned hardwoods species and are higher than reported values for MDF or OSB boards, or wood-polymer composites (Najafi and Khademi-Eslam, 2011), since it does not contain synthetic adhesives or hydrophobic polymers in composition, as well as due to the hydrophilic nature of cellulose and hemicellulose, which seems to be enhanced after dissolution and precipitation.

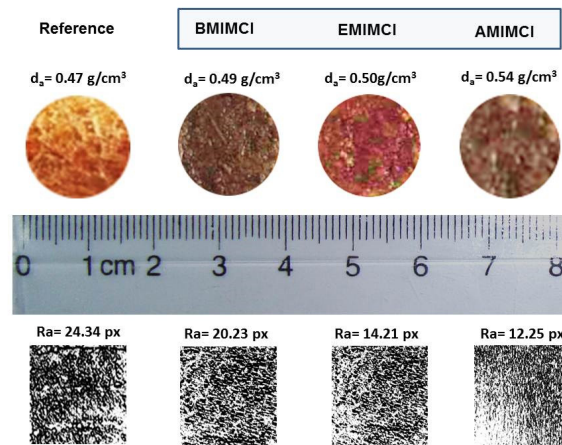


Figure 3.14. Obtained wood composites: photographic images, apparent densities, and computed roughness profile (Croitoru and Patachia, 2014)

For this type of wood composites, the higher the density (implicitly the fraction of lignocellulosic binder for the sawdust particles), the lower the water uptake values and therefore the lowest relative volume modifications due to swelling. The pattern of water uptake suggests a possible two-step process, in which about half of the final absorbed water occurred in the first two days of water contact with the wood. This is followed by a period of very slow but ongoing slight water uptake. In the first step, rapid water uptake and swelling of the compressed wood particles at the surface of the composite occurs, while the second absorption step occurs at a lower rate, involving the swelling and diffusion of water into the volume of the composite (through the compressed wood sawdust particles and precipitated lignocellulose from the surface, which may act as a barrier).

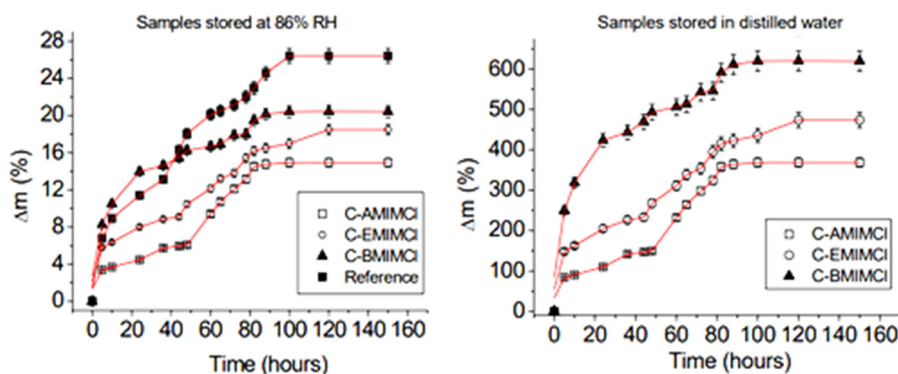


Figure 3.15. Water uptake kinetic of the wood composites and reference (Croitoru and Patachia, 2014)

Regarding the mechanical performance of the composites in initial (dry) state, it has been observed (Figure 3.16) that they are more resistant in the first stage of compression (until 60% of their initial thickness) due to their high compactness, as a result of the precipitated lignocellulose that binds the wood particles together, thus the composite being able to oppose more resistance to compression. The highest resistance to compression has been recorded for the composite that was obtained with AMIMCl, probably due to the higher amount of lignocellulose binder.

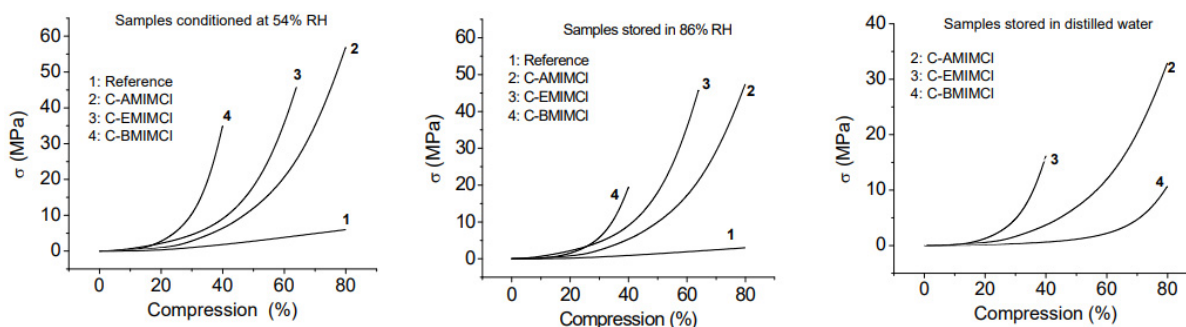


Figure 3.16. Water uptake kinetic of the wood composites and reference (Croitoru and Patachia, 2014)

For the composites stored at 86% relative humidity, it can be observed that at 80% compressive strain, the compression strength decreases with about 15%, by comparing to the reference, for which a 50% decrease is registered. This behaviour could be explained considering that water has a plasticizing effect on the cellulose matrix. Based on the capacity of the ionic liquids to swell and dissolve lignocellulose, as well as the property of water to precipitate it, a better contact and adhesion between undissolved wood particles can be attained. The adhesion of wood particles by the precipitated lignocellulose is responsible for low surface roughness and high dimensional stability of the composite material.

Taking into account that traditional wood composites obtaining technologies involve toxic monomers, phenol-based resins and organic solvents, the method which I have developed uses alkylimidazolium chlorides as solvents or dispersing media and could contribute to the protection of the environment.

3.6. Polymer nanocomposite materials obtained with ionic liquids

Carbonaceous nanomaterials, especially nanotubes (CNTs) could be nowadays accounted as the most promising fillers for polymer composites, due to their high aspect ratio as well as their unique optical, mechanical, thermal, electrical and gas barrier properties (Savvas et al., 2016; Tasis et al., 2006). They are reported to efficiently tune both the surface and bulk properties of polymer composite materials at relatively low CNT: polymer ratios (0.1-1% wt.), which could deem them useful as antistatic, reinforcing, radiation-stabilizing, flame-retardant agents or as compatibilizers in composite materials designing (Cao et al., 2015; Sangermano et al., 2008). However, when using CNTs difficulties could arise from their low dispersibility in solvents and incompatibility with most thermoplastic polymers (Ferreira et al., 2016).

Another research direction I have developed is related to the obtaining and functionalization of carbon nanotubes in ionic liquids through short-period irradiation with a continuous wave diode laser ($\lambda = 970$ nm) of graphite targets submerged in ionic liquids. The resulted IL-functionalized multiwalled carbon nanotubes (MWCNTs) show good compatibility with thermoplastic polymer matrices such as HDPE.

The advantages of using this graphite laser ablation method reside in the obtaining of MWCNTs and the achievement of their functionalization in one step, thus eliminating further work steps related to CNTs isolation,

dispersion, treatment with functionalization agents, or using toxic volatile organic solvents such as toluene, dimethylformamide, dimethyl sulfoxide and so forth.

CNTs functionalization in ionic liquids

The graphite targets have been submerged in two types of ionic liquids, namely 1-butyl-3-methylimidazolium tetrachloroferrate (BMIMFeCl₄) and trihexyltetradecylphosphonium chloride (TTDPCI) (weight ratio of graphite: IL= 1:15) (Figure 3.17). Laser irradiation of the IL/MWCNTs dispersions was performed with a continuous wave diode laser ($\lambda = 970$ nm), with a defocused spot (2.5 mm) at a power density of $P_d = 5\text{ kW/cm}^2$ for a determined time period (10s).

After laser irradiation, the resulted dispersions were diluted with toluene, and the resulting functionalized MWCNTs were separated by ultracentrifugation, re-immersed in toluene until complete removal of leftover ILs. The functionalized nanotubes derived from the phosphonium IL are abbreviated as *TTCl-MWCNTs* and the nanotubes derived from the alkylimidazolium IL as *BFeCl-MWCNTs*.



Figure 3.17. Photographic images of the ILs, of the resulted MWCNTs/IL dispersions and the structural formulas of the phosphonium and imidazolium ILs (unpublished results, [PNII-RU-TE-2014-4-0173 final synthetic report, 2017](#))

The survey XPS spectra of the BFeCl-MWCNTs (Figure 3.18) proves the grafting of the BMIM⁺ imidazolium moiety, through the N1s peak centered at 399 eV ([Okpalugo et al., 2005](#)), as well as of the FeCl₄⁻ anion (through the presence of Cl-specific 2p_{1/2} peak centered at 236 eV and of both Fe 2p_{3/2} and 2p_{1/2} specific peaks centered at 712 eV and 730 eV) ([Xun et al., 2015](#)). The XPS spectra of TTCl-MWCNTs reveal the presence of the grafted phosphonium-derived moieties, through the peaks characteristic to both P and F (Figure 3.19) ([Blundell and Licence, 2014](#)).

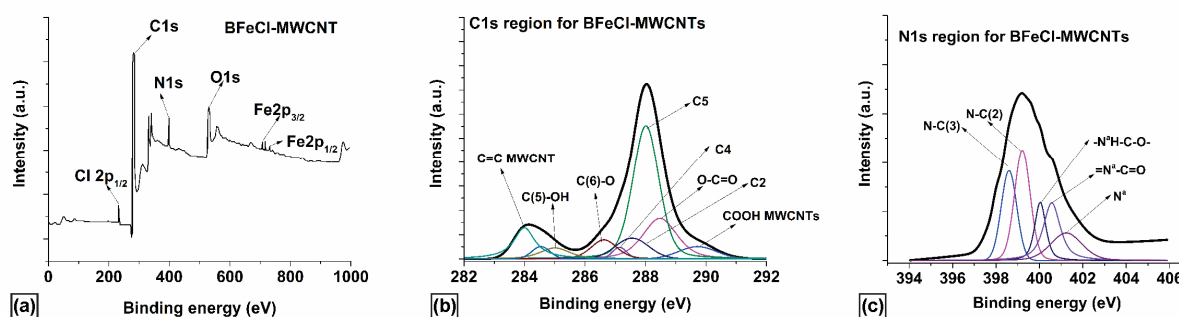


Figure 3.18. Survey XPS spectra and high-resolution details for C1s and N1s envelopes of BFeCl-MWCNTs (unpublished results, [PNII-RU-TE-2014-4-0173 project final synthetic report, 2017](#))

Supplementary, an insight in the C1s region of the XPS spectra for both TTCl- and BFeCl- MWCNTs prove the presence of carbon associated with the alkylimidazolium cation (C4, C5, C6), respectively with the alkylphosphonium cation (C1', C6', C7'). Also, the N1s region (Figure 3.18c), for BFeCl-MWCNTs reveals the

presence of nitrogen from the original alkylimidazolium cation (N^+), as well as of several instances of nitrogen, linked to partly oxidized carbon atoms. ($=N=O$ or $NH-C-O-$) (Foelske-Schmitz et al., 2011).

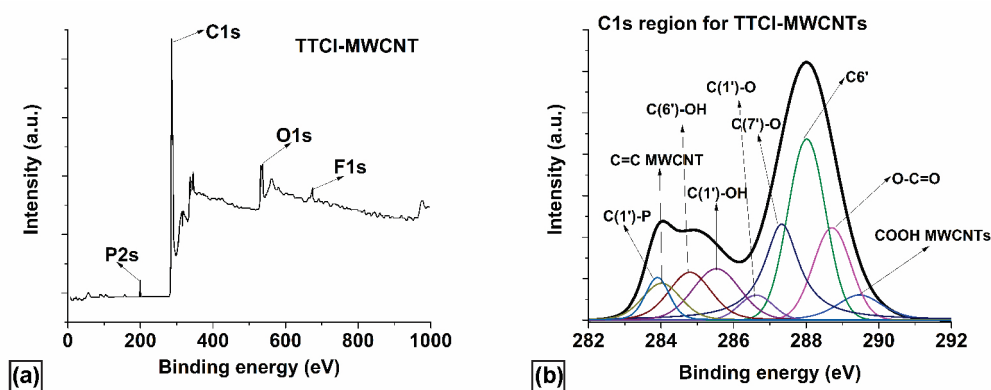


Figure 3.19. Survey XPS spectra and high-resolution details for C1s envelope of TTCl-MWCNTs (unpublished results, PNII-RU-TE-2014-4-0173 project final synthetic report, 2017)

A type of esterification reaction between the partly oxidized MWCNT surface and the partly oxidized IL cations seems to take place. This esterification grafting mechanism could be confirmed through both the presence of the $O-C=O$, $C(6)-O$ and $C(7')-O$ peaks in the C1s region of the XPS spectra from Figure 3.18 and 3.19, at ~ 289 eV, as well as through the carbon atom-instances present in the mentioned region, ascribed to the ionic liquids cations. Hydroxylation of the ionic liquid cation seems to be sustained by the C1s XPS spectra, due to the presence of $-OH$ groups associated with the carbon atom occurrences that are specific to the alkylimidazolium (such as $C(5)-OH$, $C(6)-O$), respectively the alkylphosphonium cation ($C(6')-OH$ and $C(1')-OH$).

Functionalized MWCNTs/HDPE polymer nanocomposites obtaining and characterization

The functionalized HDPE/MWCNT composites have been obtained through the HDPE and MWCNTs mixture in toluene casting and solvent evaporation method, as previously described by Goyal et al. (Goyal et al., 2016).

Briefly, to different determined volumes of 5 wt.% functionalized MWCNTs dispersion in toluene, a fixed amount of HDPE powder (previously grounded in a planetary mill at $-80^{\circ}C$; < 0.5 mm average particles diameter) has been added stepwise under continuous magnetic stirring and refluxing at $90^{\circ}C$, until total dissolution of the polymer occurred (5 hours).

The obtained dispersion has been cast in glass Petri dishes (the volume of the dispersion has been kept constant, respectively 8 mL) and the toluene has been evaporated at $40^{\circ}C$ and 10 mbar in a vacuum drying oven for 5 hours.

The amounts of MWCNTs functionalized with both ILs were 0.4 % wt. (samples coded *HDPE/TTCl-MWCNTs 0.4*; *HDPE/BFeCl-MWCNTs 0.4*) and respectively 0.8 % wt. (samples coded *HDPE/TTCl-MWCNTs 0.8*; *HDPE/BFeCl-MWCNTs 0.8*) reported to the polymer.

Surface functionalization of nanotubes with the selected ionic liquids has determined a better relative dispersibility of these materials in toluene as well as in the thermoplastic polymer matrix, by comparing the SEM micrographs from Figure 3.20 to other similar micrographs comprising of nanocomposites obtained with raw MWCNTs through different synthesis methods, as reported in the reference literature (McNally et al., 2005; Tang et al., 2003).

The TTCl-MWCNTs seem to be more uniformly embedded in the thermoplastic polymer matrix, probably due to their dominantly hydrophobic character, imparted by the long alkyl chains from the IL-derived moiety, in comparison to the BFeCl-MWCNTs which seem to possess a lower adhesion to the matrix. The lower dispersibility degree of BFeCl-MWCNTs in HDPE could be due to their higher surface polarity, imparted by a

synergy between the shorter alkyl chain and its possible partial conversion to more dominantly polar C=O and/or C-OH groups.

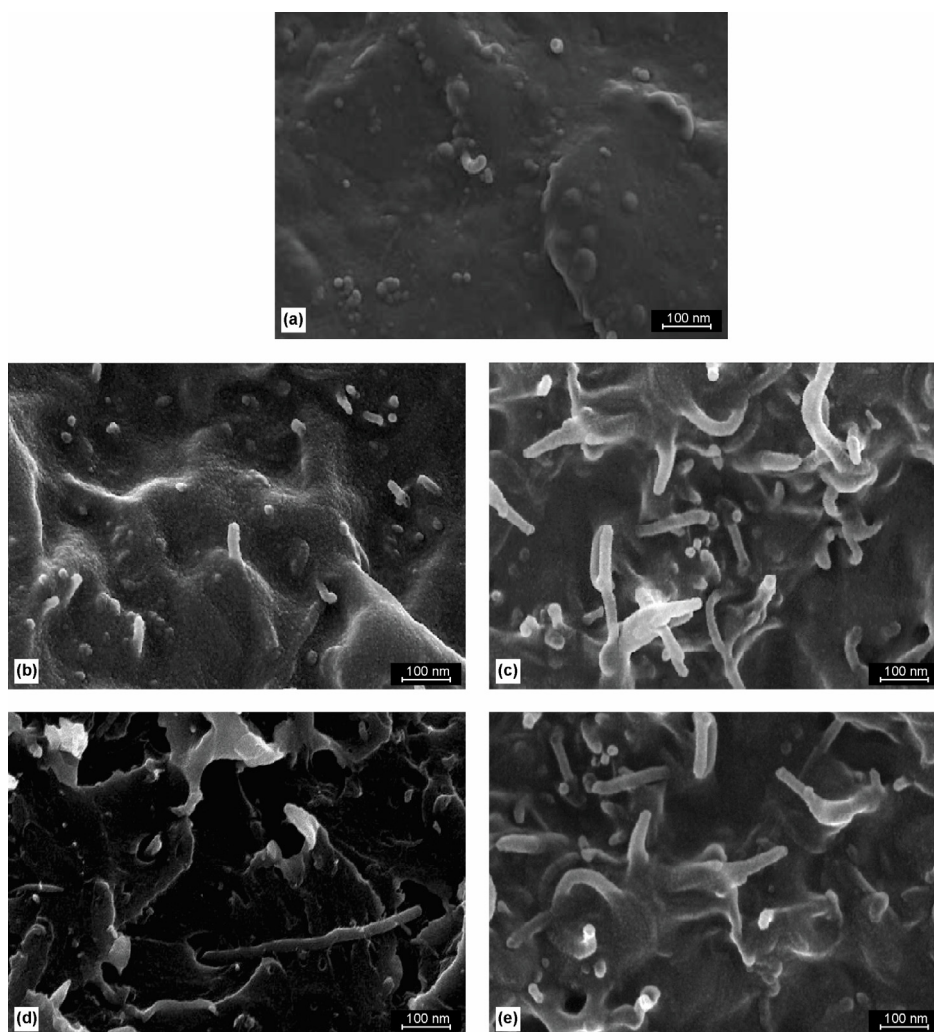


Figure 3.20. Cross-sectional SEM micrographs of (a) HDPE; (b): HDPE/BFeCl-MWCNTs 0.4; (c): HDPE/BFeCl-MWCNTs 0.8; (d): HDPE/TtCl-MWCNTs 0.4; (e): HDPE/TtCl-MWCNTs 0.8 (unpublished results, [PNII-RU-TE-2014-4-0173 project final synthetic report, 2017](#))

The obtained functionalized MWCNTs can efficiently tune the surface properties of the HDPE as a function of their functionalization type and loading amount, without significantly altering the texture of the polymer. The nanotubes functionalized in 1-butyl-3-methylimidazolium tetrachloroferrate can decrease the surface energy of HDPE with up to 56%, making them useful in applications where otherwise the low polarity of HDPE would present a bottleneck, such as adhesion, coloring, painting and so forth.

3.7. Composite cellulose aerogel materials via ionic liquids for hydrogen storage applications

Much effort has been dedicated to finding efficient alternative technologies for storing hydrogen as a lightweight, compact energy carrier for mobile applications. Up to date, there are several technologies involved in hydrogen storage, such as storage in liquid or compressed gas state or solid-state storage. Storage of hydrogen in liquid and compressed gas state is economically inefficient while also possessing a non-negligible security risk. Thus, an emphasis has been set on developing solid-state technologies based either on chemical or physical sorption of H₂ on high surface area adsorbents.

The solid-state sorbents should pose specific material properties, such as a minimum of 6.5% wt. sorption capacity at temperatures and pressures near the standard ones (25 °C, 1 atm), 65 g/L volume capacity, combined with low cost and non-toxicity. To date, efforts are being performed to find the optimum material to meet all of the criteria mentioned earlier.

Ionic liquids have attracted significant attention due to their use in catalysis-related applications and as "green" solvents for a large variety of polymers and gaseous compounds (CO, CO₂, NO_x, CH₄, superior hydrocarbon analogues, and so forth). Their unique physicochemical properties have also determined their usefulness in hydrogen storage systems, either by using a low molecular weight unsaturated IL as hydrogen storage material, either as an inert solvent, as a catalytically active solvent, as a co-catalyst, or as a stabilizing agent for catalyst nanoparticles (Lombardo et al., 2019; Sahler and Prechtel, 2012). Stracke and co-workers have determined the hydrogen sorption properties of an alkylimidazolium ionic liquid, namely 1-alkyl (aryl)-3-methylimidazolium N-bis(trifluoromethanesulfonyl)imidate in the presence of palladium loaded on active carbon (Pd/C) or Ir catalysts, and determined a 30 g/L of hydrogen adsorption yield (10% wt.) at 1 atm, which is twice that compressed hydrogen gas can attain at 350 atm (Stracke et al., 2007).

I developed an original idea for testing the applicability of ionic liquids in hydrogen storage applications in the frame of the European Research Infrastructure H2FC (Integrating European Infrastructure to support science and development of Hydrogen and Fuel Cell Technologies towards European Strategy for Sustainable Competitive and Secure Energy, FP7-INFRASTRUCTURES-2011-1, Grant Agreement No 284522) project at the National Center for Scientific Research "Demokritos" from Athens, Greece.

The idea of this project was to study the hydrogen storage properties of two ionic liquids, 1-allyl-3-methylimidazolium chloride (AMIMCl), and 1-butyl-3-methylimidazolium chloride (BMIMCl), loaded into cellulose aerogels in the presence of a Pd/C catalyst (10% wt. Pd loading on active carbon).

I have obtained the aerogel materials through controlled IL elimination from cellulose-IL solutions by adding a non-solvent (water), followed by water elimination through freeze-drying, so as the final material will have an IL loading of 30% and a Pd/C catalyst loading of 10%. A series of two references were used: (1)- neat cellulose aerogels, without Pd/C and ILs in composition, and (2)- cellulose aerogels loaded with Pd/C, but with the ILs completely removed from their structure.

For the accurate characterization of the hydrogen storage properties of the obtained materials, several H₂ adsorption measurements (volumetric, gravimetric) under different temperature (25 and 100 °C) and pressure (1-100 bar) conditions were performed by the personnel at the HYSORB facility of National Center for Scientific Research "Demokritos" in Athens- Greece.

The main aim was to investigate all materials' H₂ storage capacity under different pressures (1-20 bar at 298 K). Measurements were performed using two volumetric systems (the high-pressure PCTPro-2000 and the low-pressure Quantachrome AS1) and ultrapure (99.9999 %) hydrogen gas. In all cases, a certain amount (appr. 600-800 mg for high-pressure measurements and appr. 200 mg for low-pressure ones) of each sample had to be degassed under ultra-high vacuum (10⁻⁶ mbar) for at least 24 h. In the high-pressure measurements, volume calibrations with helium gas were performed before each measurement, using inert non-sorbing samples with the same skeletal volume as the composite materials examined.

Interestingly, the aerogel with AMIMCl showed a relatively increased hydrogen uptake (ca. 0.3 wt.%) compared to the low Pd loading in the sample (10 wt.%), pointing to a 500% enhancement at room temperature, which is considered a noticeable result, encouraging further studies.

Chapter 4. Polymeric gel materials via ionic liquids

4.1. Polymer gels as functional materials: synopsis and motivation

Polymer gels represent a unique class of porous materials, intermediate between conventional solids and liquids, containing a diluted and crosslinked polymeric matrix phase in a continuous fluid medium that shows no steady-state equilibrium flow.

Typically, these materials can be found in a swollen state resulting from the equilibrium between the osmotic forces and the crosslinked polymer network (Ibrahim et al., 2018). The osmotic forces that result from the difference in chemical potential between the chemical species inside the gel and those from its outside environment are accountable for these materials' plethora of applications. Typical applications are in the domain of energy (electrolytes for batteries or fuel cells), biomedicine (e.g., controlled delivery devices, shape memory artificial membranes, wound healing devices), sensors (e.g., pH sensors, light sensors, heavy metal ions sensors), environment protection (adsorption media for pollutants) or as scaffolds/precursors for other types of porous materials (Bahram et al., 2016; Shibayama, 2017). The relaxation (extension) of the polymer macromolecules leads to the extensive swelling ability of these materials, which in some cases can reach as much as 10 to 20 times their own (initial) weight (a swelling degree of 100 to 200 %).

Crosslinking, which ultimately renders the material insoluble, could be performed chemically (i.e., by introducing covalent bridging points in the network, either through crosslinkers capable of reacting with the functional groups present in the macromolecular backbone or through high-energy irradiating of the polymer (g. UV, γ radiation, and so forth) (Duquette and Dumont, 2019) or physically (by inducing reversible entanglement points, i.e., crystallites in the network, through hydrogen, electrostatic or dipole-dipole bonding of adjacent macromolecular chain regions) (Lv et al., 2019). Physical crosslinking, which could be performed either through cryostructuring (i.e., submitting the polymer to alternated freezing and thawing cycles) or through modifying the ionic strength of the polymeric system, has the advantage of being more environmental-friendly, avoiding the use of potentially toxic crosslinkers (Croitoru et al., 2020a; Croitoru et al., 2020b; Fernández et al., 2010). Crosslinking (chemical or physical) is responsible for the stability of these materials in different fluid media. Simultaneously, their swelling ability depends mostly on the hydrophilic functional groups that the starting monomer/polymer building block possesses, either inherently or through functionalization (Zhang et al., 2015). Typical hydrophilic functional groups include -OH, -COOH, -NH₂, -CONH₂, -CONH-, and -SO₃H.

Nowadays, most of the polymers used in gels manufacture are synthetic (e.g., poly (vinyl alcohol) (PVA), poly (acrylic acid) and its derivatives (PA), poly (ethylene glycol) (PEG) or poly (2-hydroxyethyl methacrylate) (PHEMA)) (Klekiel et al., 2020). However, the need to minimize as much as possible the strain put on the environment using non-renewable resources has re-bought to focus biopolymers as building blocks for gel materials (Crescenzi et al., 1997).

Biopolymers are generally widely available, non-toxic, environmentally-friendly, cost-efficient. They could be used either as a total replacement of synthetic polymers in the manufacture of hydrogels (alone or in various blends and composite formulations) or as blends, composite mixtures, and grafts with synthetic polymers. In the latter case, biopolymer addition is beneficial because it could improve or even impart new properties to the gel, such as adhesion, hydrophilicity, swelling capacity, net ionic charge, affinity towards different target compounds, permeability, biodegradability, and so forth, without further employing functionalization reactions or other additives (Crescenzi et al., 1996)

Among biopolymers, polysaccharides (cellulose, β -glucans, glycans) and polysaccharide derivatives (carboxymethylcellulose, cellulose acetate, chitosan, alginates, chondroitin sulfate, xanthan, carrageenan, etc.)

have been widely used as such in the manufacture of hydrogels or combination with various synthetic polymers (Croitoru et al., 2020b; Magnani et al., 2000).

Water-swallowable polymers are generally called *hydrogels* and were first reported in 1960 by Wichterle and Lím (Wichterle and Lím, 1960). By definition, water must constitute at least 10% of the total weight or volume of a gel in order for it to be considered a hydrogel. Hydrogels also possess a degree of flexibility very similar to natural tissue due to their significant water content.

I have been involved since the beginning of the PhD program in 2006 in the obtaining and characterization of PVA-based hydrogel materials, synthetic PVA-biopolymer blend or composite hydrogel materials or biopolymer hydrogel materials. While the synthesis and obtaining of gels using water or conventional organic compounds as solvent/dispersing medium has been widely studied, ionic liquid-aided obtaining or processing of polymer gels (be they of synthetic or natural origin) is still an incipient domain which constitutes one of my topics of interest as a research domain.

The results presented in this chapter are focused on two directions: (1) – the obtaining and applications of hydrogel materials through the complete dissolution of biopolymers (wood biomass, i.e., lignocellulose) in ionic liquids followed by physical crosslinking, and (2) – the behavior of “traditional” hydrogels based on synthetic polymers (such as PVA) in different types of alkylimidazolium ionic liquids.

4.2. Polymer gels obtained with ionic liquids

Due to their high dissolution ability for biopolymers, ionic liquids (especially those comprising alkylimidazolium or alkyipyridinium cations, but also some new amino acid-derived ones) could serve as excellent means for obtaining polysaccharide (cellulose, chitosan, chitin, etc.) or protein (silk, fibroin) gel architectures with potential applicability as biomedical materials or as sorbent materials for environment remediation (Silva et al., 2012).

Due to the difference in dissolution and processing operational conditions, non-water-soluble hybrid synthetic/natural polymer hydrogels are generally difficult to obtain, and the weight ratio between the two polymer components of the material is usually limited. Usage of ILs in this domain enables the facile obtaining synthetic/natural polymer hydrogels with new functional properties. For example, through using choline-based low toxicity ionic liquid, superior biocompatible electroconductive hydrogels have been obtained as bioactive scaffolds for excitable tissues, such as neural or cardiac muscle tissues, without the incorporation of potentially toxic metallic nanoparticles, carbon nanotubes, or inorganic electrolytes (Noshadi et al., 2017). If the gel is desired to function in water, the ionic liquid can be later exchanged for this solvent.

Another advantage of using ionic liquids in hydrogels obtaining resides from the facile functionalization of the polymers (both in homogeneous or heterogeneous phase) by the ionic liquid itself, without supplementary agents. The material's rheological properties, hardness, and mechanical properties can be widely modified using ionic liquids with tunable architectures (by variation of the cation and anion type) (Jastram et al., 2021). In some innovative approaches, ionic liquids containing unsaturated (polymerizable) cations can be converted into polyelectrolyte gels, usually by radical polymerization (Claus et al., 2020).

4.2.1. Lignocellulose hydrogels: structure and applications

Most studies up to date employ the use of ionizing radiation (such as γ radiation) or chemical crosslinkers (such for example dicarboxylic acids, dialdehydes, epichlorohydrin, initiator-mediated grafting of unsaturated moieties) to obtain polysaccharide or polysaccharide/protein hybrid hydrogels. While bearing satisfactory efficiency, often

these methods of crosslinking pose themselves a potential detrimental environmental effect, due to their inherent toxicity (Ahmed, 2015).

A *novel direction of research* which I have developed is to obtain stable (ligno)cellulose-based hydrogels through a physical crosslinking method, namely *cryogelation* (the application of alternate freezing and thawing cycles) (Roata et al., 2018), already successfully applied in obtaining poly (vinyl alcohol)-based hydrogels (Hassan and Peppas 2000; Patachia et al., 2011). This method of crosslinking does not imply the addition of potentially toxic crosslinkers or intrusive solvents into the system and removes the additional purification step (unreacted traces of monomers, crosslinkers, solvents and so forth). This method has not been applied before in obtaining cellulose or lignocellulose-derived gels. After their obtaining, the ionic liquid from the structure of the gels was exchanged from the bulk of the material with water, resulting a dimensionally-stable and porous hydrogel material. The characterization of the wood lignocellulose gelation mechanism and the correlations between the structure of the material and its properties *could be deemed also an additional original contribution of this research direction on the application potential of ionic liquids in materials science and engineering.*

In the study I have conducted, the hydrogels were obtained starting from solutions of Norway spruce wood (*Picea abies*) sawdust dissolved in 1-butyl-3-methylimidazolium chloride (BmimCl) ionic liquid in a 10% wt. basis. The homogeneous solutions obtained were submitted to five alternative freezing-thawing cycles, with the following parameters: freezing temperature: -50°C, thawing temperature: room temperature (21°C), freezing and thawing duration: 24 hours each. The number of alternate freezing/thawing cycles has been chosen to take into consideration that a lower number of cycles does not ensure the satisfactory stability of the gel to solvent action. Transparent lignocellulose hydrogels have been obtained, as shown in Figure 4.1. The hydrogels were then immersed in distilled water, and the BmimCl ionic liquid was removed from the structure of the material.

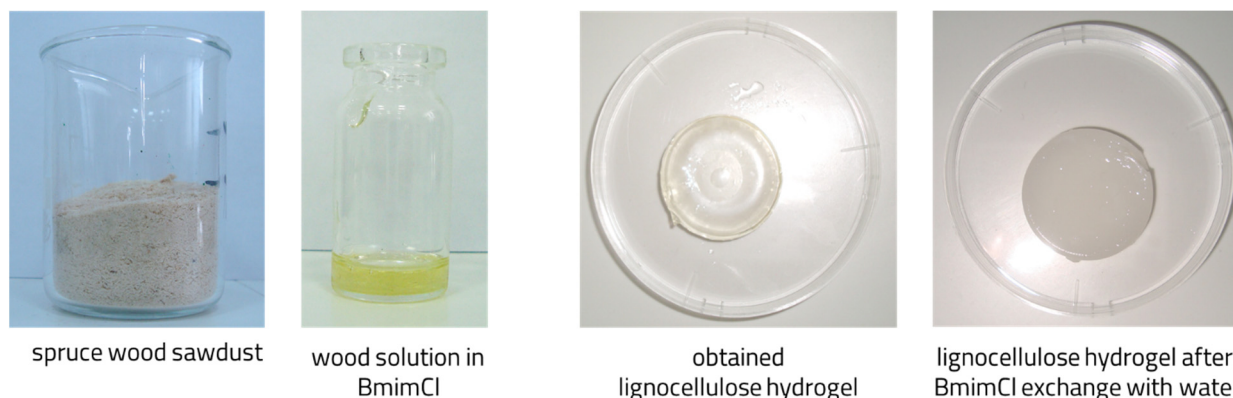


Figure 4.1. Photographic image of the starting materials and the obtained lignocellulose hydrogels

The microstructure of the lignocellulose hydrogel contains a heterogeneous distribution of macropores (dimensions of 10-180 μm) (Figure 4.2a). Since BmimCl is a good solvent for cellulose, the obtained hydrogel is already in a “swollen-state”. Immersion in water determines a collapsing of the gel structure, as indicated by the SEM micrograph from Figure 4.2b. The micropores average reduction in diameter at water immersion spans from 20% to 70%, compared to the original swollen hydrogel. Furthermore, the region in contact with water (the top layer ca. 150 μm thick) has a granular appearance, determined by the precipitating of lignocellulose, after the ionic liquid leakage from this area. This collapsed region creates a diffusional barrier which has a dominating influence on the permeation rate of different chemical species in/from the gel, as well as on the sorption mechanism (da Silva Burgal et al. 2016). The presence of the diffusional barrier could prove useful in applications such as controlled delivery, separations of different compounds or as absorptive media (due to the high partition coefficient between the ionic liquid and water).

The obtained hydrogel is dominantly amorphous (crystallinity index of 21.11%), in contrast with the spruce wood starting material (crystallinity index of 38.21%) (Figure 4.2c). In the XRD diffractogram of the lignocellulose

hydrogel, the peaks corresponding to the cellulose I anomer (the (101) and the (040) diffraction planes, respectively), disappear, leaving only the broad (002) contribution, characteristic of cellulose II (Croitoru et al., 2011a; Stanton et al., 2018). As previous research on poly (vinyl alcohol) cryogels has indicated, the gelation may be induced by macromolecules concentrating close to each other during the slow freezing of the lignocellulose solution in BmimCl, which leads to the promoting of highly ordered regions where the polymer chains interact strongly via hydrogen bonding from the hydroxyl groups. These ordered regions (crystallites) can remain intact on the following thawing, acting as crosslinking points in the network (Figure 4.2d).

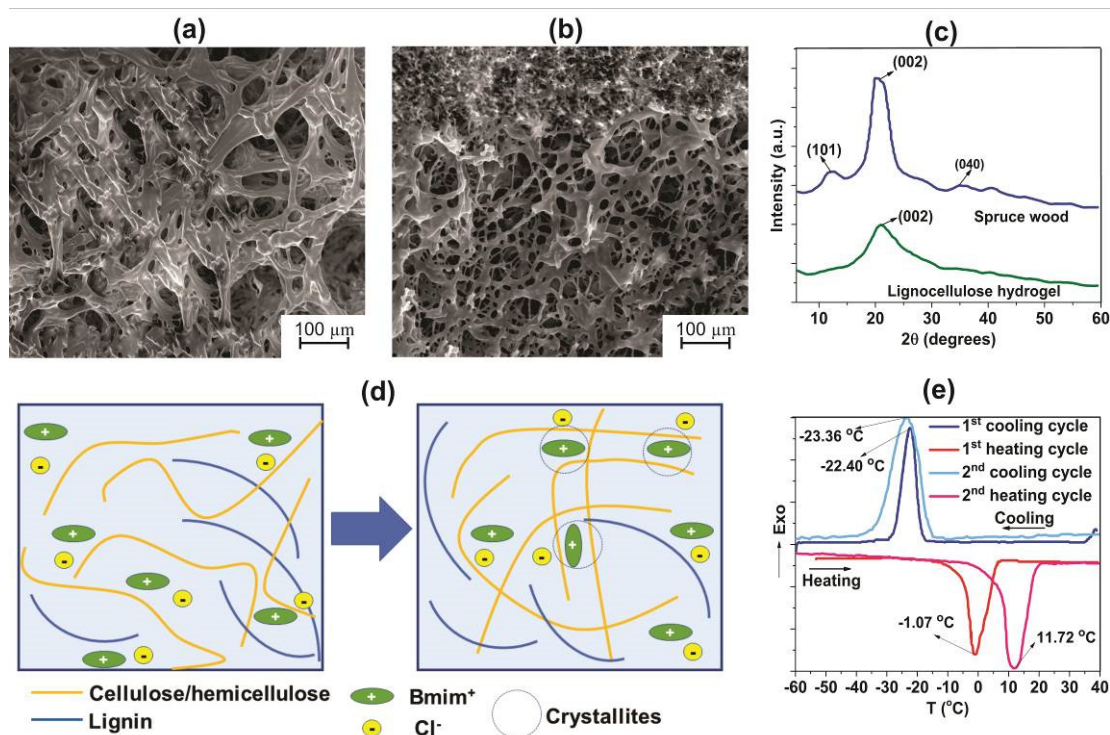


Figure 4.2. SEM micrograph of (a) neat lignocellulose hydrogel; (b) hydrogel after collapsing in water; (c) XRD diffractogram of spruce wood and lignocellulose hydrogel; (d) gelation mechanism; (e) DSC thermogram of lignocellulose/IL solution (Roata et al., 2018)

While the melting point of pure BmimCl has been reported at 76–78°C, the lignocellulose solution in BmimCl presents an exothermic crystallization peak centered at -22.4°C (on the cooling curve of the 1st cycle), due to solute-solvent interactions. Melting of the lignocellulose solution occurs at -1.87°C (endothermic peak on the 1st cycle heating curve illustrated in Figure 4.2e). Upon cooling the solution for the 2nd cycle, a shifting of the crystallization peak to lower temperature (-23.36°C) subsequent with its broadening has been observed. The broadening in the case of the second cycle occurs due to the presence of lignocellulose with a variable degree of crosslinking. It could be seen that while heating the lignocellulose for the second time, a shifting of the melting temperature to 11.72°C occurs, which could represent an indication of physical crosslinking points in the system. The system is fully thermoreversible (i.e., it can be remelted and later re-gelled) useful for example when the recycling of the ionic liquid is desired, or in the case of recovery of the sorbate (i.e., in case of using the hydrogel as sorption media).

The conducted studies have indicated that the lignocellulose hydrogels could prove useful as sorption media for heavy metal ions and dyes in environment-remediation applications. Good adsorption capacities have been recorded for Cu²⁺ (542.85 mg/g), Pb²⁺ (475.34 mg/g) and bemacid blue model anionic dye (445.98 mg/g), higher than most research conveying biomass-derived gels (Zhou et al., 2012).

Two common adsorption models (Freundlich -Eq. 4.1- and Langmuir -Eq. 4.2) have been fitted with the experimental data on the adsorption of Cu²⁺, Pb²⁺, respectively bemacid blue from aqueous solutions (Table 4.1).

$$\frac{c_e}{q_e} = \frac{1}{K_L \cdot q_{max} - c_e} \quad (4.1)$$

In Eq. 4.1, c_e is the equilibrium concentration of the metal ion in solution (mg/L), q_e is the adsorbed amount at equilibrium (mg/g) while K_L (L/mg) and q_{max} (mg/g) are Langmuir constants related to energy of adsorption and maximum uptake per unit mass of adsorbent, respectively.

$$q_e = K_F \cdot c_e^{1/n} \quad (4.2)$$

In Eq. 4.2, K_F is the Freundlich constant corresponding to adsorption capacity ((mg/g)·(mg/L)^{1/n}) and n represents a dimensionless heterogeneity factor for the adsorption sites.

Table 4.1. Parameters for tested adsorption isotherm models (Roata et al., 2018)

Adsorbate	Freundlich isotherm				Langmuir isotherm		
	q_{max} (mg/g)	K_F (mg/g)·(L/mg) ^{1/n}	1/n	R ²	q_{max} (mg/g)	K_L (L/mg)	R ²
Cu ²⁺	600.462	9.289	0.702	0.996	598.897	0.247	0.985
Pb ²⁺	654.172	8.062	0.781	0.994	600.154	0.166	0.987
Bemacid blue	486.520	3.535	1.125	0.987	478.354	0.105	0.981

The correlation coefficients from Table 4.1 (R^2) have showed that the Freundlich isotherm model is able to fit the data in a more satisfactory manner, as this type of isotherm describes multilayer physical adsorption on media with heterogenous sorption sites, as opposed to the Langmuir isotherm model (homogenous surface, monolayer adsorption). The affinity of the adsorbate for the substrate is dictated by the K_F values, indicating preferential sorption in the order Cu²⁺> Pb²⁺> bemacid blue. The 1/ n values are smaller than 1 for the heavy metal ions, indicating a good affinity of the adsorbate for the substrate, while for bemacid blue, the 1/ n value indicates a less favorable adsorption, probably due to the interaction of the bulky dye anion with the ionic liquid cations.

4.2.2. Behavior of poly (vinyl alcohol) hydrogels in ionic liquids

The main properties of hydrogels, such as density, sorption and diffusion capacity, mechanical, optical and electrical properties are determined by their water content. Hydrogels exhibit a high degree of swelling in aqueous environment. In the presence of organic solvents as well as of ionic aqueous solutions or liquid ionic compounds, the hydrogels could shrink or swell, modifying their water content and, as a consequence, all their properties (Patachia and Croitoru, 2015a; 2015b; Zhang and Cremer, 2006).

The determination of swelling behavior of hydrogels in different environments is significant because, in many applications, hydrogels come in contact with organic or inorganic ionic substances, such as in wound dressing, drugs, and protein delivery, artificial tissues, muscles or other organs, separation processes by sorption or diffusion, sensors design, etc.

As a model polymer, I have used poly (vinyl alcohol), due to its exceptional properties such as non-toxicity, non-carcinogenicity, water-solubility, biodegradability, biocompatibility, good mechanical and optical properties. Loaded with ionic substances, PVA could be a suitable matrix for electrolytes that could be used in electrochemical systems. The electrical stability of these systems is affected by the water (solvent) volatility. The replacement of aqueous or organic solvents of electrolytes that imbibe the PVA hydrogels with room temperature ionic liquids could be a promising way to obtain solid-like electrolyte materials (Patachia et al., 2011).

One of the aims of this research direction was to monitor and understand hydrogels' behavior in the presence of ionic liquids and water and to study the influence of this behavior on the system's rheological properties.

The PVA hydrogels were prepared by repeated freezing and thawing cycles. The hydrogel sample preparation has been started from a 12% PVA solution in water. The obtained PVA solution has been cooled to room temperature, then it has been molded in a Petri dish and submitted to 3 repeated cycles of freezing at -20°C for 12 hours, and thawing at room temperature another 12 hours. The obtained white and opaque PVA gel has been immersed in distilled water for 7 days, at room temperature (25°C), to allow the swelling of the prepared samples until reaching their swelling equilibrium.

The completely swollen PVA hydrogels have been cut into circular samples, pre-weighed (m_x), immersed in aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF_4) with various concentrations (12, 50, 75%, and respectively 100%), and their mass (m_t) was determined at determined time intervals until equilibrium reaching.

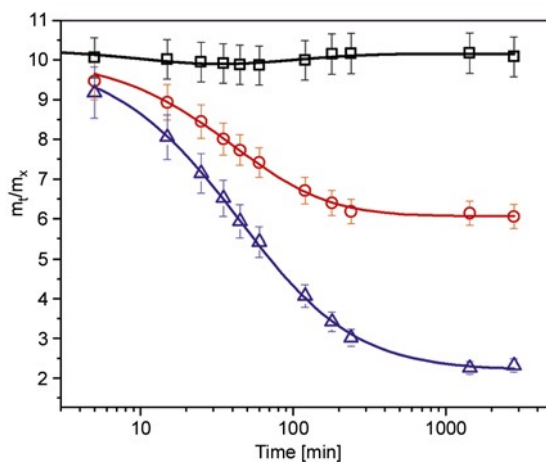


Figure 4.3. Shrinking process- PVA hydrogel normalized mass dependency as a function of time and concentration of BmimBF_4 aqueous solution: () 12%; (o) 50% and (Δ) 100% of IL (the dependences were fitted with Eq. 4.3) (Patachia et al., 2011)

By immersing the PVA hydrogels in BmimBF_4 aqueous solutions, it could be noticed that the gels shrink (collapse). The shrinkage is influenced by the IL concentration (correlated with the water activity) and the contact time. Figure 4.3 shows that higher IL concentration and contact time result in higher hydrogel mass loss and shrinking rate, and longer time of swelling equilibrium reaching has been noted. The PVA gel collapse could be explained by the water elimination from the gels' mass due to the high osmotic pressure created by IL ions from the contact solution. The sigmoidal shape of the curve describing the shrinking process for PVA gels immersed in 12% BmimBF_4 aqueous solution suggests that there are two simultaneous fluxes of matters in the system: one is that of the water leaving the initially swollen gel, and the second one is that of the IL ions that diffuse into the gel. Firstly, due to IL ions' osmotic pressure outside the gel, the water molecules, more mobile, will diffuse from the gel, determining its mass loss. Later, IL ions, more extensive and less mobile, will penetrate the gel network, determining the mass increase. Once the ionic liquid concentration inside the gel is zero, the osmotic pressure will govern the water release process.

For more concentrated BmimBF_4 solutions, the higher osmotic pressure within the gel determines a higher and more rapid water release, emphasized by a higher gel's mass loss. The sorption of IL ions into the gel will diminish due to the decrease of gel porosity due to collapsing. Also, IL ions' tendency to agglomerate at a higher concentration than 50% could be a cause of their sorption decrease. In this case, the simultaneous processes are less visible on the gravimetric kinetic curves, the IL sorption being negligible by comparison to the water release. To characterize the shrinking/collapsing behavior of PVA hydrogels in contact with ionic liquids aqueous solutions, I have participated in designing a phenomenological equation (Eq. 4.3) that considers both fluxes (of IL and water).

$$y = \frac{y_0}{\left(1 + \frac{t}{t_0}\right)^p} + y_1 \frac{\left(\frac{t}{t_1}\right)^p}{\left(1 + \frac{t}{t_1}\right)^p} \quad (4.3)$$

where $y(t)$ is m_t/m_x , t is time expressed in minutes, the values related to the water flux are represented by index 0 and those of the second flux of IL into the gel by index 1; t_0 and t_1 are the characteristic time for which a significant mass change has been noted due to the water or IL flux, respectively, and p is a power-law exponent. The coefficient y_0 shows the initial gel's swelling equilibrium that is approximately the same for all the samples. Higher t_0 values for more concentrated IL solutions pointed out that the water release, monitored in the first moments by the osmotic pressure, is counterbalanced by the IL ions sorption on the gels' surface, leading to an apparent time lag of mass change, determined by gravimetric methods. The higher the IL solution concentration is, the more significant apparent time lag is because of the increased amount of the sorbed IL ions.

The increase of t_1 parameter with the IL solution concentration increase shows the IL sorption extension to the higher contact times of the IL solution with the PVA gel, diminishing its weight loss determined by water release. The y_1 parameter represents the value of shrinking equilibrium, showing an increase with the IL solution concentration decrease. Eq. 4.3 fits very well the experimental data from Figure 4.3.

A schematic depiction of the processes that occur when the PVA hydrogel material is in contact with BmimBF₄ is illustrated for ease of understanding the involved phenomena (Figure 4.4). It could be assumed that BmimBF₄ acts as a dehydrating agent for the swollen PVA hydrogels. So, if the practical interest is to load the PVA hydrogel with BmimBF₄, a highly diluted IL solution for the gel immersion must be used. When hydrogel drying is the goal, it must be immersed into pure BmimBF₄.

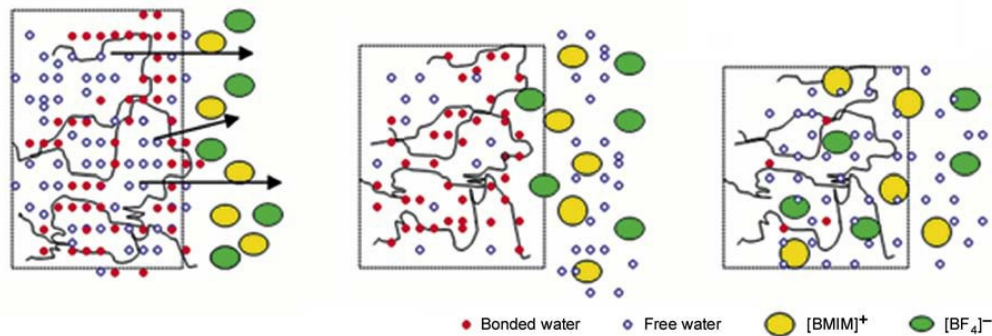


Figure 4.4. Schematic depiction of the processes that occur at the PVA hydrogel contact with BmimBF₄ (Patachia et al., 2011)

Experimental data show that the PVA hydrogel shrinking in ionic liquids and the absorption of the ions into the gel matrix strongly influence their rheological properties. Figure 4.5a shows that the values of the storage modulus, G' , are higher than that of the loss modulus, G'' , evidencing a solid-like behavior of the collapsed PVA hydrogels. The plateau modulus, G_p , (determined as the storage modulus at a frequency of 1 Hz), is lower in comparison to the G_p value of the non-collapsed PVA gel if the concentration of the IL immersion solution is lower than 50% (Figure 4.5b). This behavior could be correlated with the plasticizing effect of the absorbed cations that is predominant at lower values of the IL concentration, while, at the same time, the volume of the sample is not shrinking significantly in this concentration range.

In IL solutions having a concentration value between 12% and 50%, the storage modulus of the collapsed PVA hydrogels begins to increase, but its value is still lower than the G_p value corresponding to the initial PVA hydrogel. This behavior could be correlated to IL ions' tendency to agglomerate, decreasing the concentration of the free cations. The lower the concentration of the free cations in solution, the lower the cations absorbed and the lower the plasticizing effect marked out. At a concentration of the IL solution higher than 50%, the shrunk PVA hydrogels' storage modulus becomes higher than the value of the neat PVA hydrogel. This behavior could be explained by the increase of the cation agglomeration, which induces the decrease of their absorption and,

consequently, a decrease of the plasticizing effect; additionally, the ions, placed at the interface of the swollen PVA chains, determine a more substantial collapse of the hydrogel.

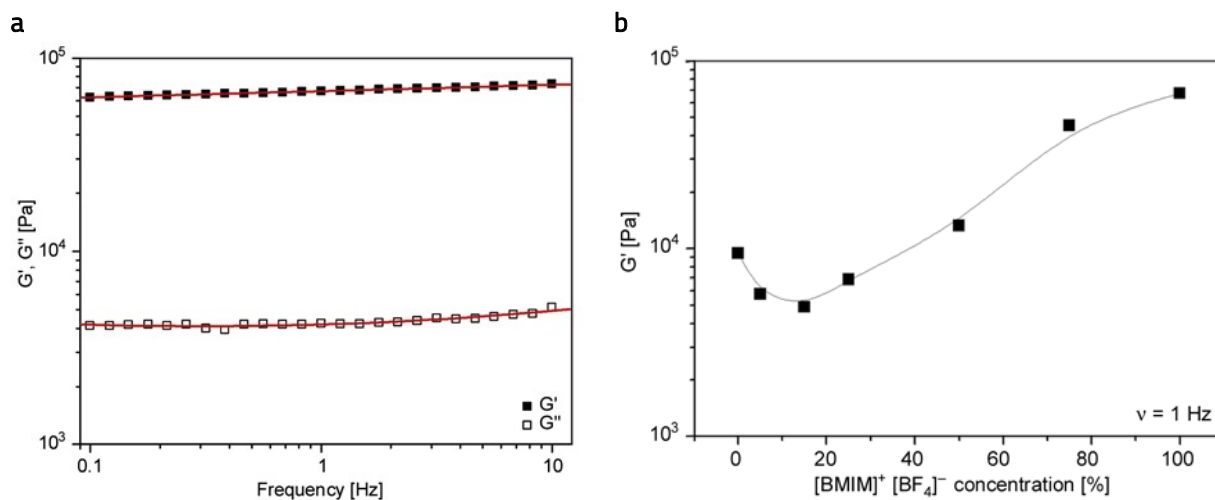


Figure 4.5. (a) dependency of the rheological parameters on the frequency, for the PVA hydrogels shrunk in pure BmimBF₄; (b) dependency of the plateau modulus G_p [G' (1 Hz)] on the IL solution concentration (Patachia et al., 2011)

The PVA hydrogel shrinking is determined by the IL ions' capacity to extract the water molecules from the hydrogel, expressed by the anions' kosmotropic (water structuring) character. The elimination of the water molecules from the gel and the higher interaction between the polymer chains determines the increase of the gel rigidity.

As concerning the interactions between the polymer and this ionic liquid, (BmimBF₄) it can be noticed that no new absorption bands appeared in the FTIR spectra, compared to neat PVA and the ionic liquid, emphasizing that no chemical interaction occurs between PVA and BmimBF₄ (Figure 4.6). The presence of the IL ions in the gel matrix, proportional to the ionic liquid solution's concentration, indicates the PVA gels' capacity to retain ions. FTIR spectra of PVA/IL gels evidence the alteration of some absorption bands due to the interaction between the components and changing system composition.

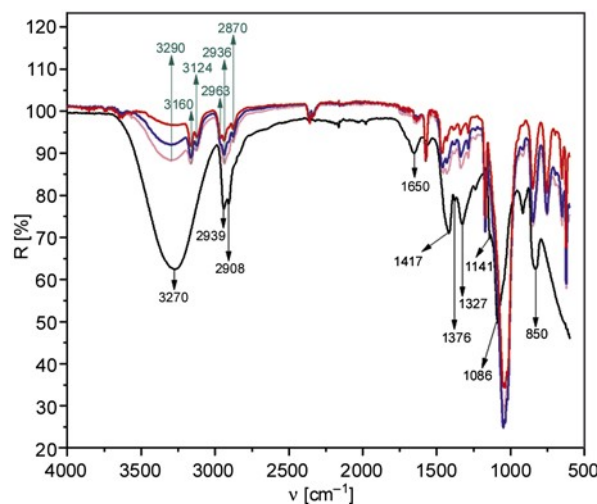


Figure 4.6. Schematic depiction of the processes that occur at the PVA hydrogel contact with BmimBF₄ (Patachia et al., 2011)

The absorption band from 3270 cm⁻¹ could be attributed to the O–H bonds from PVA, and those from the bonded water remained in the system after the gel's partial drying. When the IL concentration into the contact solution increases, a decrease of the -OH band intensity was noted. This decrease signifies that IL ions extract the bonded

water molecules from the PVA gel matrix. The characteristic band for BF_4^- from 1060 cm^{-1} is split into three peaks and shifted to 1048 , 1034 , and 1017 cm^{-1} , showing the lowering of B-F vibration symmetry due to the F atom involving within H bonds with water molecules.

Also, the skeletal and -C-O- stretching band from 830 cm^{-1} of PVA is shifted in the PVA/IL gels to 844 and respectively 848 cm^{-1} , indicating a stiffening of the polymeric chain as a consequence of the interaction by H bondings between the -OH groups of PVA.

Phenomenologically, using different analytical techniques, it has been determined that the physically-crosslinked PVA hydrogels (and generally, this behavior could be linked to other related hydrophilic polymer hydrogels) at contact with IL solutions of lower concentrations favor the IL ions sorption into the gel. IL presence determines the gels plasticizing by their crystallinity decrease.

At higher IL solution concentration, the gels' substantial collapse (shrinking) determines the decrease of the IL's ions sorption. This behavior determines the bonded water molecules' transformation into free water molecules, making the water release from the gel during the heating much more facile. The removal of bonded water determines a higher interaction between the polymeric chains and, consequently, the increase of the gel rigidity.

Conclusions

In the outline of the habilitation thesis, I have presented my research results obtained after the completion of my PhD program in 2010, regarding the applicability of ionic liquids as auxiliaries (solvents with high dissolution and washing ability, carriers) or additives to improve several properties of polymer and polymer matrix composite materials (compatibility between component phases, surface polarity, dimensional stability to water action, stabilizers, biocidal agents). The outlined domains of application for ionic liquids spans from biopolymers (cellulose, wood, chitosan, natural resins, etc.) to synthetic polymers (poly (vinyl alcohol); polyolefins). In some cases, the beneficial role of these ionic liquids can be achieved by mere compounding. The ionic liquids mentioned in this habilitation thesis have a relatively simple structure, are commercially available, and are relatively inexpensive.

Chapter one contains information regarding ionic liquids and their applicability in polymer materials engineering. Despite their excellent application potential, ionic liquids have been mainly used as solvents for polymers, as media for chemical functionalization of polymers (due to their high swelling and dissolution ability), or fractionating agents for more efficient use of biomass. There are considerably fewer studies regarding the use of ionic liquids as additives for polymeric materials and the aim of my research was to fill this gap by enlarging the research database in this domain.

Chapter two presents an outline of the original research results I had obtained starting from 2010 (when my postdoctoral internship was approved) regarding the application potential of ionic liquids in correlation with different simple or more complex polymeric systems.

- Alkylimidazolium ionic liquids can be used as UV stabilizers for biopolymer materials (cellulose, wood). Accelerated UV weathering tests (performed with UV-C radiation) have indicated that ionic liquids convert native cellulose in a more thermodynamically and oxidation-resistant form, namely cellulose II. The UV-stabilizing effect seems to be correlated with the ionic liquid's ability to be retained at the surface of the material. In this respect, hydrophobic ILs (with hydrophobic cations, anions, or both) seem to offer the best UV stabilizing effect on polymer materials. The best UV-stabilizing effect was achieved for ILs with hexafluorophosphate anions and hexyl lateral alkyl chains from the multitude of ionic liquids that I have tested. I have demonstrated that these compounds do not act as sunscreens since they are optically transparent in the 240-800 nm domain, but instead, they interfere with the free radicals that initiate and propagate the UV degradation.
- Alkylimidazolium ionic liquids can also be used to stabilize wood and cellulose against ionizing β -radiation by converting native cellulose to cellulose II, interfering with the radical mechanism involved in the degradation of lignin (for wood) and preferentially degrading themselves (forming active radical imidazolium cationic moieties) rather than the polymeric substrate. As in the case of UV radiation, more hydrophobic ILs have an increased β -radiation protection ability. The active radical imidazolium cationic moieties could be grafted to cellulose through IL irradiating, providing grafts that tune the surface properties and the dimensional stability of these materials.
- Alkylimidazolium ionic liquids with hydrophobic anions (hexafluorophosphate and tetrafluoroborate) can be used as high-performant antistatic additives for wood, while at the same time improving the material's resistance to water action. ILs with hydrophilic anions (chloride or tetrachloroferrate) provide a higher surface electrical conductivity, but can be more easily leached out of the material with time.
- Ionic liquids can act successfully as plasticizers for cellulose and wood materials. ILs determine the structural rearrangement of the cellulose macromolecules while also serving as spacers between them. The plasticizing effect can be proven by the increase in the elongation at break for cellulose with up to

180% and up to 200% for wood, aiding in their processability (it is known that cellulosic materials are rather stiff). However, ILs do not act out as traditional polymer plasticizing agents, only enhancing the elongation at break (due to the cations disrupting the intermolecular bonds between macromolecules, but also increase the tensile strength of the material (through macromolecular structural rearrangement). An increase with up to 30% of cellulose's tensile strength and 200% for wood has been noted.

- Ionic liquids can act as antifungal agents for polymeric materials that are prone to be used as substrates for such organisms (especially biopolymers). While the antifungal character of ILs has been proven since the mid 90's, there are no studies concerning such character for simpler and commercially available ionic liquids. Hydrophobic alkylsulfonium and alkylphosphonium ILs have been demonstrated as efficient antifungal agents against *Postia Placenta* (brown rot fungus).
- Ionic liquids exposed to ionizing radiation (high-energy electron beams) can act per se as functionalization agents for cellulose (nano)fibers due to the formation of active (and partly oxidized) radical cation species, which can graft themselves to the hydroxyl groups of cellulose. This grafting could impart several useful properties to cellulosic materials, such as improved compatibility with thermoplastic polymer matrices, antifungal character, UV-stability, and so forth.
- Due to their high solvation and swelling ability for polymers and dispersion agent for inorganic particulate compounds, ionic liquids can serve as solvents and carriers for obtaining organic and inorganic coatings on polymer materials. When relating to wood, moisture-stable coatings that impart high hardness to the material can be obtained by thoroughly soaking it in a polymer/IL solution or dispersion, followed by water precipitation. Using ILs as solvents and carriers, the use of toxic monomers, resins, or metal-organic precursors can be avoided, and a wood type with inferior quality can be brought up to the properties of more expensive and less-available species.
- Alkylimidazolium ionic liquids can be used in restoration of cellulosic artifacts by merely washing the material with a diluted aqueous solution of the IL. The plasticization effect of the ILs can be used to restore flexibility to the brittle artifact while improving its tensile (rupture) strength. The high solvation ability of the ILs could help remove different degraded binders and sizers and stains, contributing to the preservation and restoration of the cultural heritage.

Chapter three presents an outline of the original research results I regarding the application of ionic liquids as multipurpose additives for obtaining polymer composite materials with functional properties.

- The idea of using a single type of IL to impart a better compatibility between the phases of a composite material, while at the same time providing stability to water, to UV radiation or to other degrading factors of biological origin is a novel one, and has not been explored previously in conjunction with ionic liquids. Long-chain alkylphosphonium and alkylammonium ionic liquids can be efficiently used to improve the compatibility between polar organic reinforcing agents (wood, cellulose fibres, carbon nanotubes) or fillers (inorganic particles, such as marble, talcum, etc.) and thermoplastic (polyethylene, polypropylene) polymer matrices.
- Ionic liquids with high polymer solvation ability can be used to obtain "all-polymer" composites (a polymer acting as a filler/reinforcing phase, while another (or the same) polymer serving as the matrix). A new type of composites was obtained with alkylimidazolium chloride ionic liquids, resembling the principle of agglomerated wood boards. The advantage of such composite materials resides in the use of more environmentally-friendly polymers.
- Composite cellulose aerogels with high porosity, loaded with palladium-based catalysts and ILs, were obtained using ionic liquids (in this application, the IL has the combined role of a solvent and sorption medium). The composite aerogels can act as media for hydrogen sorption and storage. The results are still in an incipient phase, but promising results have been obtained for cellulose aerogels loaded with 1-

allyl-3-methylimidazolium chloride (relatively increased hydrogen uptake of 0.3 wt.% at room temperature).

Chapter four presents some results regarding the use of ionic liquids as solvents and porogens to obtain physically-crosslinked polymer hydrogels, and it is, basically, an extension of my Ph.D. research theme, where I have synthesized poly(vinyl alcohol) hydrogels for selective ab/adsorption of organic molecules and metallic ions from aqueous solutions.

A physical crosslinking method, namely cryostructuring (submitting a polymer solution to alternate freezing and thawing cycles), to obtain cellulose hydrogels starting from cellulose solutions in alkylimidazolium ionic liquids. These hydrogels could be used in environmental remediation applications (sorption of heavy metal ions and organic dyes), owing to their high adsorption capacity imparted by a favorable combination between their porosity and affinity (surface rich in hydroxyl groups).

This chapter assessed classical physically-crosslinked poly(vinyl alcohol) gels behavior in a model alkylimidazolium ionic liquid with tetrafluoroborate anion evaluated as a function of IL concentration. It was determined that in the IL, the hydrogels bear a complex behavior as a function of ILs solution concentration. For diluted aqueous IL solutions, the hydrogels uptake a high amount of ILs from the solution while simultaneously eliminating the water from the structure. These two fluxes of matter (ionic liquid and water) occur almost at the same rate in these conditions. When in contact with concentrated IL solutions, the hydrogels preferentially expel their structural water, collapsing significantly, and the IL absorbed amount is minimal in this case.

(B3) Evolution and development plans for career development

The defining responsibilities that I undertake as a member of the academic staff are currently based on five interconnected principles: (1) promoting student-oriented teaching activities; (2) mentoring (not just transmitting knowledge, but also principles); (3): ensuring an excellent connection to the challenges and provocations brought by the industrial environment's continuous development, (4): high-end domains research activities, and (5): instilling a passion for science and research to students.

As the next step in my academic career, as a Ph.D. coordinator in *materials engineering*, I intend to apply these five principles to developing young research teams with good performance in science, which can later be autonomous and develop research directions. "Excellence with a personal touch" as it is said.

B.3.1. Plans and development on the didactical level

I have been involved in didactical activities since 2006, firstly as associated teaching staff and starting from 2015 as a full-tenured lecturer and associate professor. I entered this teaching profession to believe that I can transmit knowledge and passion for science and research to my students. The main disciplines that I (currently) teach as a full-tenured associate professor are in the materials engineering and industrial engineering domain, namely Materials Science, Materials Technology, Materials Science and Engineering (in Romanian and English, to first year undergraduates), Ecological Materials for Welding, Statistical Process Control, Radiation Protection, and Research Projects Management.

Having a physics and chemistry background and having taught for eight years in chemistry, my approach is to "go to the fundamentals" whenever possible. I always structure my lectures and encourage my students to ask questions such as "why is this particular behaviour happening?"; "why is material X stronger than Y?"; "what can I do with...?"; "how can I choose...?", "how can I achieve...?", which I believe are fundamental for a good engineer, irrespective of the specialization.

At the next level in my career, I will be focused on continuously improving my teaching and lecturing abilities through interacting with the students and with my colleagues, as well as by participating in teacher exchange programs, as a keynote or plenary speaker at international conferences or thematic (teaching-skills oriented) workshops and seminars (including those organized periodically by my home institution).

I have gradually developed my courses over the years, considering the pace of development in the respective field and my students' and colleagues' feedback. I plan to update all of my courses and publish major revised versions at least every two years. Being a full editor of the *Journal of Materials Science* is very helpful in this respect, as we periodically write editorials on or invite review and research papers on topics with high impact in materials science and engineering.

Also, I will update the written support for each discipline's practical activities and include new attractive ones. From my experience, students appreciate course sections of the type "Did you know?" or "How it's made", with a bit of background and history behind a material, an engineering process, or concept/law, because it makes them aware of the importance of the issue and may spark potential future interests for them. I will enrich and update my courses (both the electronic support and the written material) in such sections periodically for all the disciplines I teach.

With the funds that I have attracted as project coordinator, I have improved the didactical database of the disciplines I lecture. for example, as responsible for the materials science didactical laboratory, I have enriched

the collection of materials for microscopic study, I have purchased instruments for measuring the levels of ionizing and non-ionizing radiation, model radiation sources and screens, apparatus for determining the level of toxic pollutants in the atmosphere (volatile organic compounds, NO_x , SO_x , etc.) which are useful for the disciplines I teach at the Industrial Security Engineering specialization in the frame of my faculty (i.e., Materials Science and Engineering). I will continue to participate in the quest for attracting new funds (research or didactic-oriented grants) to improve the didactical database.

I will involve undergraduate and bachelor students in didactical and research-related activities since their first years of study, including their (part-time) inclusion in the teams of future research grants. These activities could contribute to the students' future enrolment as Ph.D. candidates.

After obtaining the Ph.D. coordinating ability in Transilvania University of Brasov doctoral school, I will be actively involved in attracting Ph.D. student candidates in materials engineering. In collaboration with my colleagues, specialists in multiple fields: laser processing, thin films, coatings, materials characterization, materials processing, materials recycling, welding, additive manufacturing, process modelling, etc., I will promote the formation of a multidisciplinary and (with time) self-sustaining team of young researchers. I will mentor and encourage them to submit research projects of their own in eligible competitions.

I am aware of the defining and complex role a Ph.D. coordinator has, far beyond a relationship of employment, or achieving a research goal. I aim to develop a good professor/student relationship and bond that in time will bear good fruit: new highly-skilled and trained specialists in the domain of materials engineering.

B.3.2. Plans for research development and evolution

Based on the research experience gained since the finishing of my Ph.D. program, I aim to elaborate on the research results obtained in this period and develop new research directions in the field of materials engineering by constructing (and building on) the already existing solid collaborations with colleagues from Romanian and international research institutions. The goal in establishing new research directions is fivefold, (1): attracting potential Ph.D. students; (2): applying for new research grants in eligible competitions as coordinator or responsible; (3): involving the Ph.D. students and undergraduate students in the research teams of the granted projects whenever eligible to do so; (4): enlarging the research equipment infrastructure of the university, and (5): engaging new research collaborations with national and international peers.

B.3.2.1. New ionic liquids synthesis and assessment of their environmental impact and toxicity

Ionic liquids possess practically an unlimited possibility of tuning in terms of their solvation ability, surface tension, hydrophilicity/hydrophobicity by modifying the type or dimensions of the cations or the anions. So far, I have used commercially-available ionic liquids, but in the next step, I plan to **synthesize ILs with new structures**, building on the already available commercial compounds or starting completely from new sources, such as amino acids, peptides, betaines, alcohols, sugars or glycosidic compounds, heterocyclic plant alkaloids and so forth. The new ILs will be tested in terms of solubility for different polymer materials, as well as for the beneficial properties that they could impart on such materials. Using more environmentally friendly raw materials for ILs synthesis could lead to a lowering of the ILs price, which currently limits their widescale industrial use.

For example, my preliminary research results have indicated that alkylimidazolium ILs with modified tetrachloroaluminate or tetrachlorostannate anions can dissolve low molecular mass poly (vinyl chloride) or low-density polyethylene.

Being relatively new compounds, the potential long-term effect of ionic liquids on the environment and on human health still not well understood. In collaboration with specialists from the medical and biomaterials domain, a

research direction I want to follow is the **assessment of such long-term effects of the ILs** on the environment, which would be of real benefit to the research community. Our preliminary tests have indicated that some long-chain tetrafluoroborate alkylimidazolium ionic liquids could possess mild toxicity assessed by a 20% decrease in the germination rate of beans and radish seeds, while shorter chain halide ILs have very limited or no influence at all on the germination rate, but this information needs to be thoroughly correlated with other types of toxicity tests.

B.3.2.2. Ionic liquids as additives for non-polyolefin synthetic polymers

So far, I have used mainly polyolefins and poly (vinyl alcohol) in conjunction with ionic liquids, but I want to extend this research direction in **using other types of synthetic thermoplastic polymers** (such as poly (vinyl chloride), polyamides, polystyrene, poly (lactic acid), etc.) **and elastomers and to quantize the effect imparted on these materials by different types of ILs.**

An interesting idea I want to pursue in this direction with the specialists in 3D-printing from my faculty and my external collaborators is the obtaining of thermoplastic polymer, polymer-blend, or core-shell composite architectures as filaments for 3D-printing applications. The ILs could act as stabilizers for the polymer phase during extrusion, as lubricants and antistatic additives. Also, they can enable polymer blend combinations difficult to achieve otherwise. I have already purchased a mini filament extruder (maximum heating temperature of 250°C) and performed some extrusion tests with IL-additivated ABS (acrylonitrile butadiene styrene) copolymer, but the behavior of the material to 3D-printing is still to be assessed and many more formulations to be prepared and tested under different printing conditions. Also, ILs could act as liquid resins viscosity tuning agents and could interfere with the hardening pattern (due to their plasticizer effect) in resin 3D-printing applications. To achieve this objective, I have already pin-locked the necessary funds to buy an Anycubic Photon Mono X resin 3D printer, which permits printing maximum build volumes of 192×120×245 mm. I will use this printer also in conjunction with research direction *B.3.2.5* in the obtaining of shape-specific 3D-printed gel formulations containing ILs (commercial and custom-made).

B.3.2.3. Ionic liquids as additives for recycled polymer matrix composites

While initiating the research domain of using ILs as multipurpose additives in virgin polyolefin polymer matrix composites (Croitoru et al., 2018a), another interesting research direction that I want to pursue is related to the **obtaining of composites with recycled polymer matrices and/or reinforcing agents and using ILs as additives (compatibilizers, etc.) in these materials.**

This research direction could lead to the more efficient recycling of thermoplastic polymers (from household wastes, construction industry, automotive industry) by incorporating them in composite materials with inorganic (particulate waste from the construction industry), organic (wood, cellulose fibers, etc.) reinforcing agents, or both.

Considering the insufficient recycling rate for plastic materials (in 2015, in Romania, 70% of the total amount of municipal wastes has been disposed of in landfills), finding new possibilities of recycling that involve the embedding of polyolefin wastes in products with a higher value and higher quality becomes a priority.

Due to the recycled polyolefins lower molecular mass, lower crystallinity, and possibly the presence of oxidized surface groups, these materials could be actually more compatible with the reinforcing agents in comparison to the virgin polyolefins, and the role and influence of the ionic liquid additives in such composites needs to be redefined. Through the research funds I have attracted, I have partly ensured the required infrastructure for achieving this goal. Since 2016, I have purchased a melt flow index tester for polymer materials, a centrifugal

rotor mill for powdering of polymer wastes, a hot-press, and molds for compression molding polymer composites. In the foreseeable future, I aim to attract funds for purchasing a Brabender polymer mixing station to aid in the mixing of polymer components or between polymers and the reinforcing agents.

B.3.2.4. Ionic liquids as auxiliaries for biopolymer materials

In the frame of this research direction, **the newly synthesized ionic liquids dissolution/swelling/functionalization ability will be tested in conjunction with different biopolymers** (cellulose, biocellulose, wood lignicellulose, chitosan, chiton, proteins, etc.). We will use the biopolymer solutions or dispersions in ionic liquids to obtain **fibers through electrospinning** (ILs are organic electrolytes) or **coatings/films with fixed thickness on various substrates through spin-coating**. For this direction, I plan to attract funds in the foreseeable future to purchase an electrospinning station and a spin-coater.

B.3.2.5. Ionic liquids as solvents and porogens for hydrogels

The swelling and dissolution ability of ILs (including newly synthesized ones) for various hydrophilic synthetic polymers or biopolymers will be further exploited to **obtain hydrogels through physical** (alternate freezing and thawing cycles) or **chemical crosslinking** (addition of crosslinkers, UV light, etc.). The hydrogels could be used **as environmentally-friendly sorbent media for toxic organic compounds and heavy metal ions from wastewater**, exploiting the high polarity and surface area of the polymeric material and at the same time, the high gel/water partition coefficient for these species ensured by the IL.

The hydrogels could become the starting materials for aerogels obtaining, by replacing the IL for water and eliminating the water through subsequent freeze-drying. Aerogels could possess higher sorption abilities for different toxic chemical species, could serve as scaffolds for different types of porous biomaterials and as support for gas sorption and storage applications.

Another interesting aspect to be pursued is related to the gas adsorption capacity of different types of custom-made ionic liquids.

I aim to obtain shape-tailored hydrogels loaded with different active principles (nutraceutical or therapeutic agents) through 3D-resin printing of various liquid resin precursor-ionic liquid mixtures. The ionic liquid presence could tune the texture, rigidity and softness of the final material, aiding in obtaining a flexible gel, rather than a solid brittle crosslinked thermoset material. The additive manufacturing of hydrogels is a new and trending research domain and I believe that my research ideas could bring important contributions to this domain.

B.3.2.6. Photocatalytically-active and sorbent materials used for environmental remediation

During the 2015 till present period, I have collaborated with specialists in ceramic and metallic/ceramic hybrid coatings on physico-chemical characterization of coatings and on assessing their photodegradation efficiency towards different model organic pollutants under UV or visible radiation (Cristea et al., 2019; Croitoru et al., 2020c). I wish to continue pursuing this direction **to assess the photocatalytic efficiency of thermal sprayed, laser cladded, or magnetron sputtered coatings or films and critically assess their usefulness for environmental remediation applications (air or wastewater decontamination)**.

Also, I wish to continue the research theme started in the frame of my Ph.D. thesis, namely the **obtaining of poly (vinyl alcohol) hydrogels** with high selectivity towards different organic molecules and ions (Croitoru et al., 2020a; 2020b; Patachia and Croitoru, 2015a) by blending this polymer **with various biopolymers (with or without the addition of ILs)** and **assess their adsorption effectiveness towards different pollutants**.

I believe that the abovementioned research themes have a broad multidisciplinary degree and complement the research domains promoted by the members from the Transilvania University of Brasov doctoral school. The research themes' multidisciplinary nature could ensure fruitful future collaborations and research grants, also attracting Ph.D. candidates in materials engineering. The research grants will contribute to the enlargement of the infrastructure available to the Ph.D. students while also supporting them financially and gaining international visibility.

I also propose disseminating the research directions results, as mentioned above, through *at least* one participation per year at an international conference and publishing at least two ISI-indexed papers per year.

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