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Ionic Liquids: Versatile additives for polymeric materials and nanocomposites

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Definition and example of ionic liquids

Ionic liquids are salts constituted by organic cations and organic or inorganic anions

They usually present low melting point; some of them are liquid at room temperature

Examples of some common cations of ionic liquids.

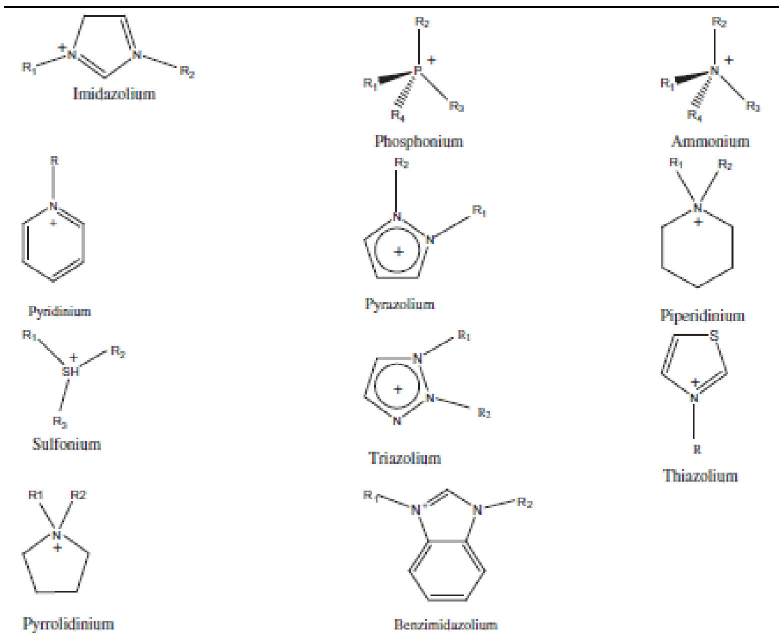
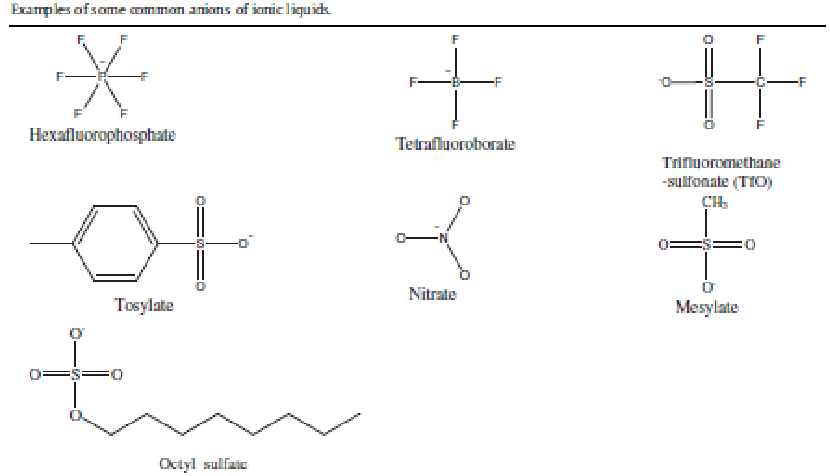


Table 2
Examples of some common anions of ionic liquids.



MAIN CHARACTERISTIC OF IONIC LIQUIDS

- ✓ high ionic conductivity
- ✓Thermal stability
- ✓Low vapor pressure
- ✓Easy preparation process

Main applications of ionic liquids

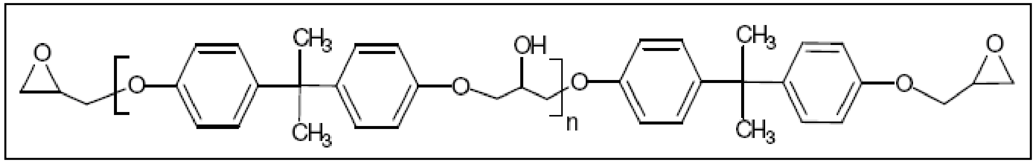
- Solvent for organic syntheses and polymerization
- Solvent for biopolymers, including cellulose
- Component for solid electrolytes
- Preparation of inorganic nanoparticles and hybrids
- Dispersion agent for nanoparticles, including carbon nanotube
- Reactive additives
- etc

SOME EXAMPLES DEVELOPED IN OUR LABORATORY

- Ionic liquid as curing agent for epoxy resin
- Ionic liquid as dispersing agent for carbon nanotube
  - Preparation of nanocomposites based on thermoplastic;
  - Preparation of nanocomposites based on thermosetting
- Compatibilizing agent of polymer blends
- Electro-rheological fluids

Ionic liquids as curing agent for epoxy resin

Epoxy resin



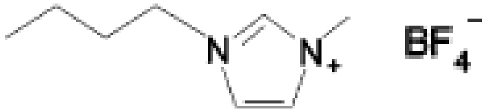
- ➢Excellent physico-mechanical properties
- ➢Thermal and chemical stability
- ➢Excellent adhesion properties
- ➢Excellent barrier properties against corrosion agents.

Main applications:
Coatings; adhesives; component for structural composites; electronic devices.

Most common Curing agent

- •Aliphatic amines (curing at room temperature)
- •Aromatic amines (curing at high temperatures)
- •Anhydrides (curing at high temperature)

Imidazol-based ionic liquid as curing agent

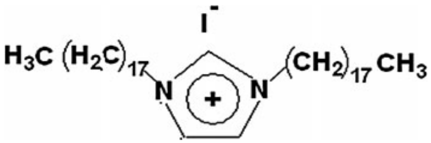


1-butyl-3-methyl-imidazxolium tetrafluoroboratre

Kowalczyk and Spychaj, Polimery 48, 833 (2003)
5% of IL – curing at 230°C

1-butyl-3-methyl-imidazxolium dicyanamide

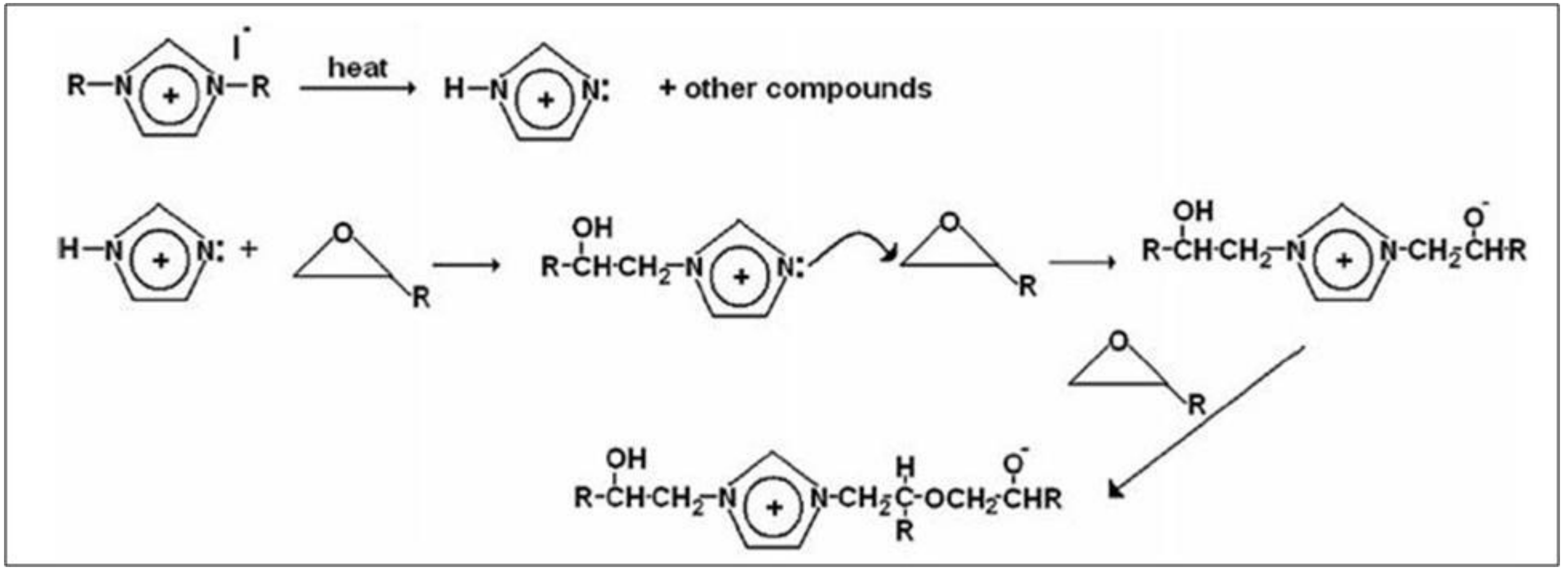
Rahmathulah et al, Macromolecules 42, 3219 (2009)
17% IL – curing at 165°C



N,N'-dioctadecyl imidazolium iodide

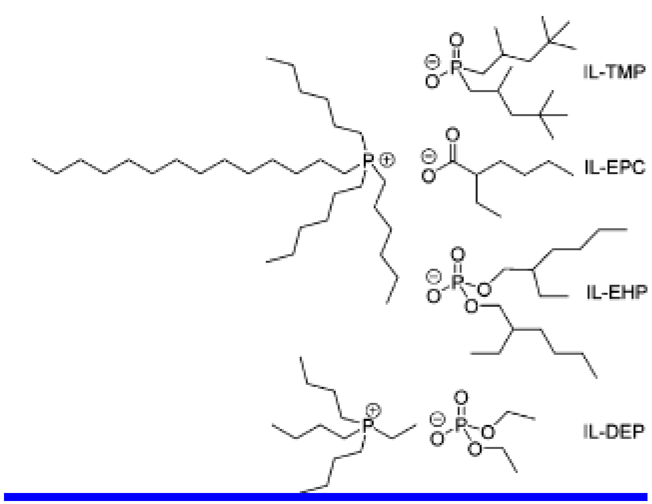
B. G. Soares et al Macromol Mater Eng 296: 826(2011)
10% IL – curing at 150°C

Imidazol-based ionic liquid as curing agent



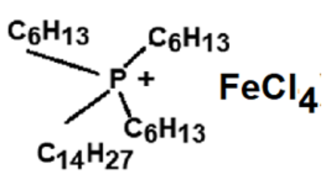
B. G. Soares et al Macromol Mater Eng 296: 826(2011)

Alkyl-phosphonium-based ionic liquid as curing agent



A. A. Silva et al Polymer 54: 2123 (2013)

Nguyen et al, ACS Sustainable Chem Eng 4: 481 (2016)



Henriques et al, ACS Appl Polym Mater. 2022, in press

Alkyl-phosphonium-based ionic liquid as curing agent

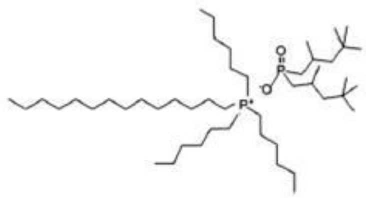
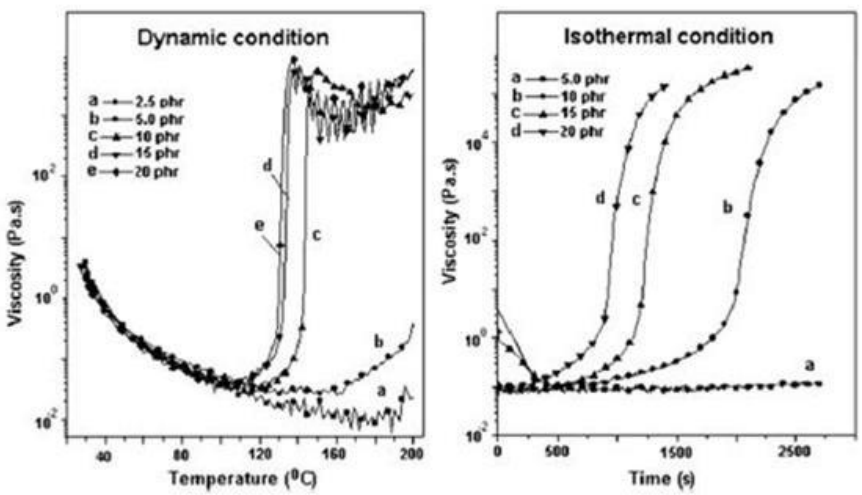


Fig. 1. Structure of trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate (IL104).



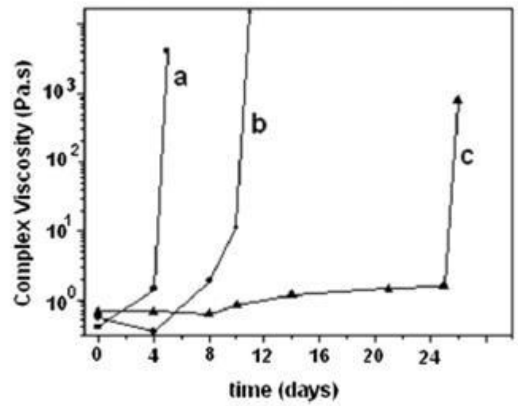


Fig. 4. Effect of the IL content on the viscosity change of the DGEBA/IL systems at room temperature. IL content in DGEBA: 10 phr (a); 5 phr (b); and 2.5 phr (c) of IL.

A. A. Silva et al Polymer 54: 2123 (2013)

Glass transition temperature of the epoxy networks cured with different hardeners

Ionic liquid			Glass transition temperature (°C)
type		Content (phr)	
D230	Aliphatic amine	32	100
MCDEA	Aromatic amine	54	160
MTHPA	anhydride	100	115
IL104	IL104	5	135
	IL104	10	145
	IL104	15	141

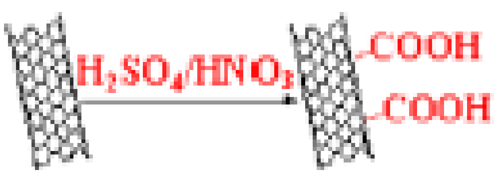
A. A. Silva et al Polymer 54: 2123 (2013)

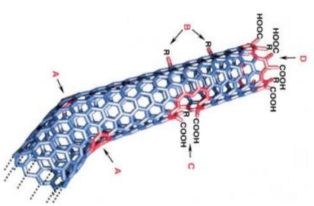
Dispersion of carbon nanotube and use in preparation of conducting polymeric composites

The dispersion of CNT in polymeric matrices is difficult due to the high tendency of CNT to agglomerate.

Surface modification of CNT to improve dispersion and compatibility with polymeric matrices

Covalent modification





Disadvantages:

•Time-consuming and expensive synthetic procedures;

•Destruction of the π-conjugation, affecting the electrical conductivity

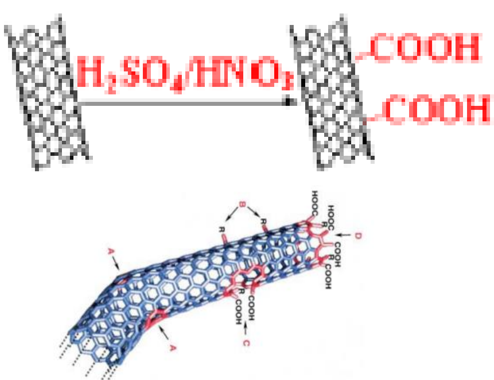
Tunckol et al Carbon 2012, 50, 4303.

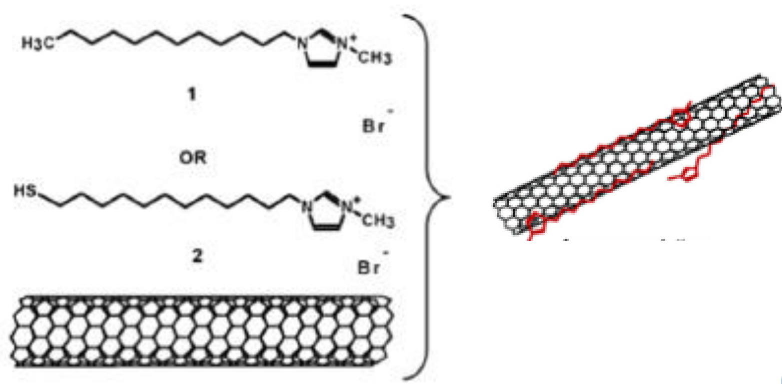
The dispersion of CNT in polymeric matrices is difficult due to the high tendency of CNT to agglomerate.

Surface modification of CNT to improve dispersion and compatibility with polymeric matrices

Covalent modification

Noncovalent modification





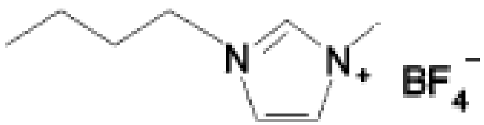
Nanocomposites based on epoxy resin

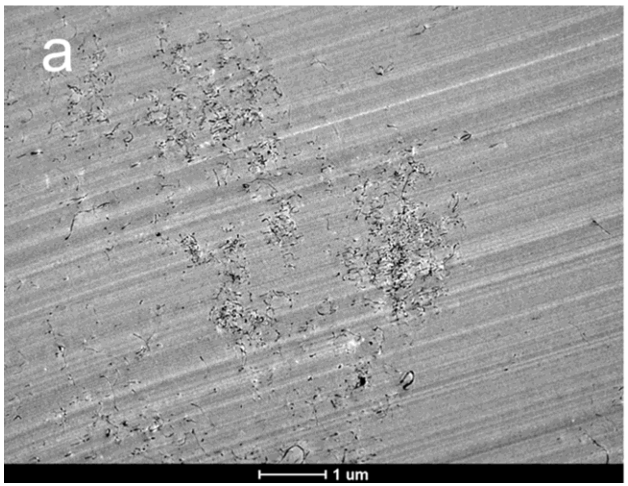
First, CNT is ground with ionic liquid in a mortar

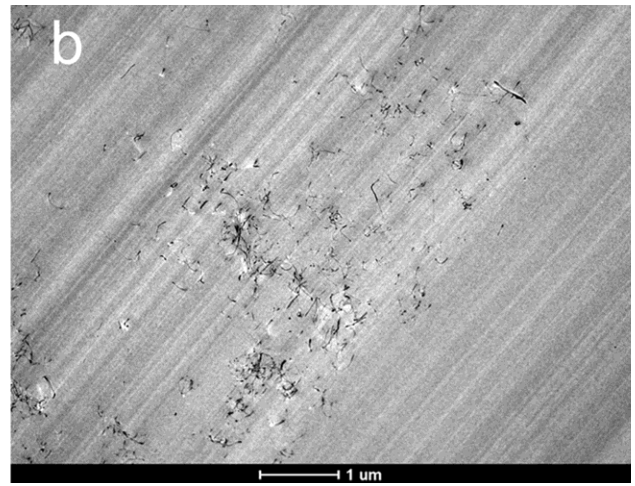
Then, the paste is blended with epoxy resin with the help of small amount of solvent to decrease viscosity and sonication

→

Epoxy/CNT cured with anhydride







1 phr CNT

without IL

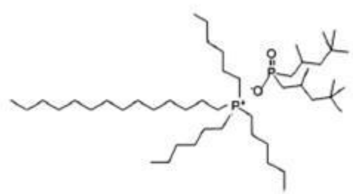
$1,0 \times 10^{-5}$ S/cm

5 phr of IL

5×10^{-3} S/cm

E.C. Lopes Pereira and B.G. Soares, J. Appl. Polym. Sci. 133, 43976 (2016)

Dual role of ionic liquid:



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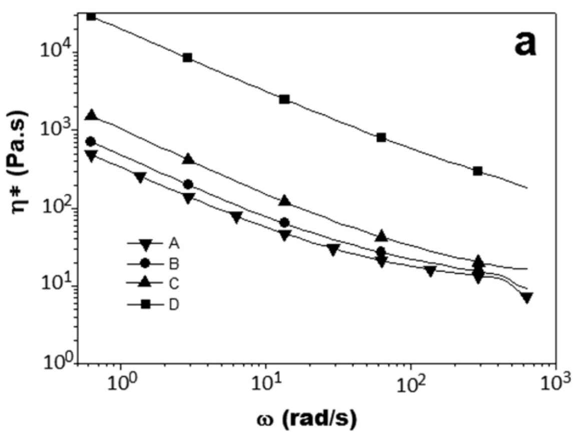
Dispersing agent for CNT
Curing agent for epoxy resin

1 phr CNT/ 10 phr IL

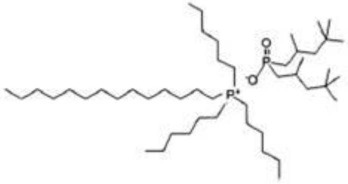


A: CNT and epoxy (high shear speed mixer), after addition of IL
B: CNT mixed with ER/IL using high shear speed mixer
C: CNT/IL previously ground in a mortar and then, blending with ER using high shear speed mixer
D: CNT/IL previously ground in a mortar; blending with ER using sonication and acetone

B.G. Soares et al, European Polymer Journal 84, 77 (2016)

Dual role of ionic liquid:

Dispersing agent for CNT
Curing agent for epoxy resin



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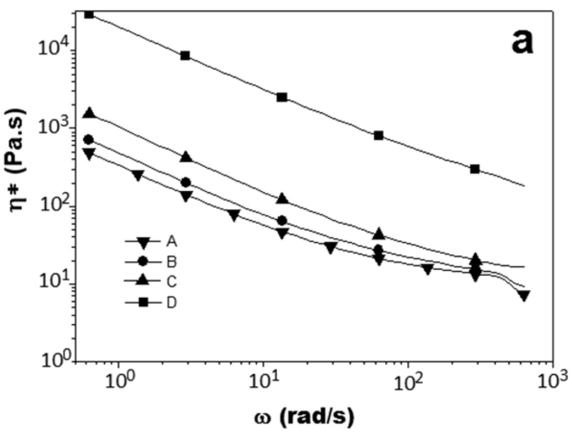

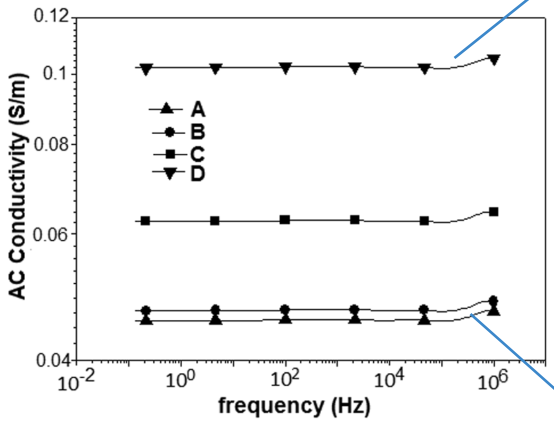

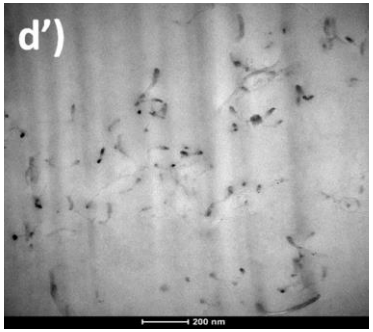

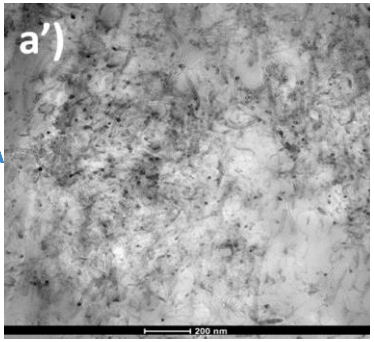

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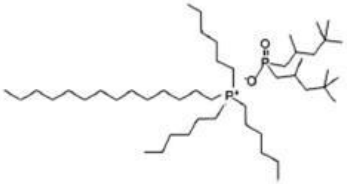

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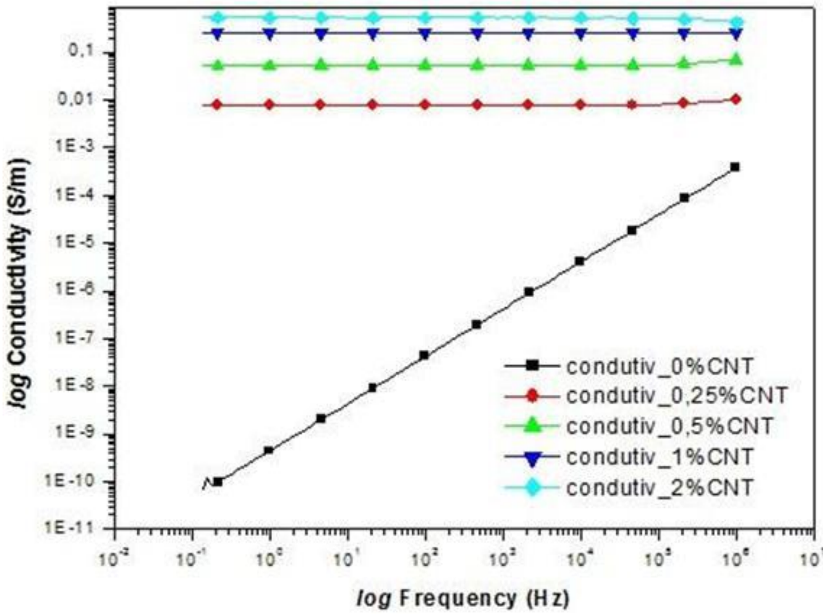
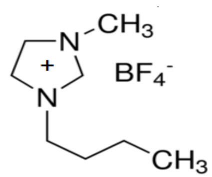
Dispersing agent for CNT
Curing agent for epoxy resin

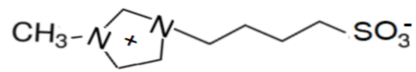


B.G. Soares et al, European Polymer Journal 84, 77 (2016)

Polyaniline/CNT hybrid prepared in the presence of IL



1-Butyl-3-methyl tetrafluoroborate (IL1)



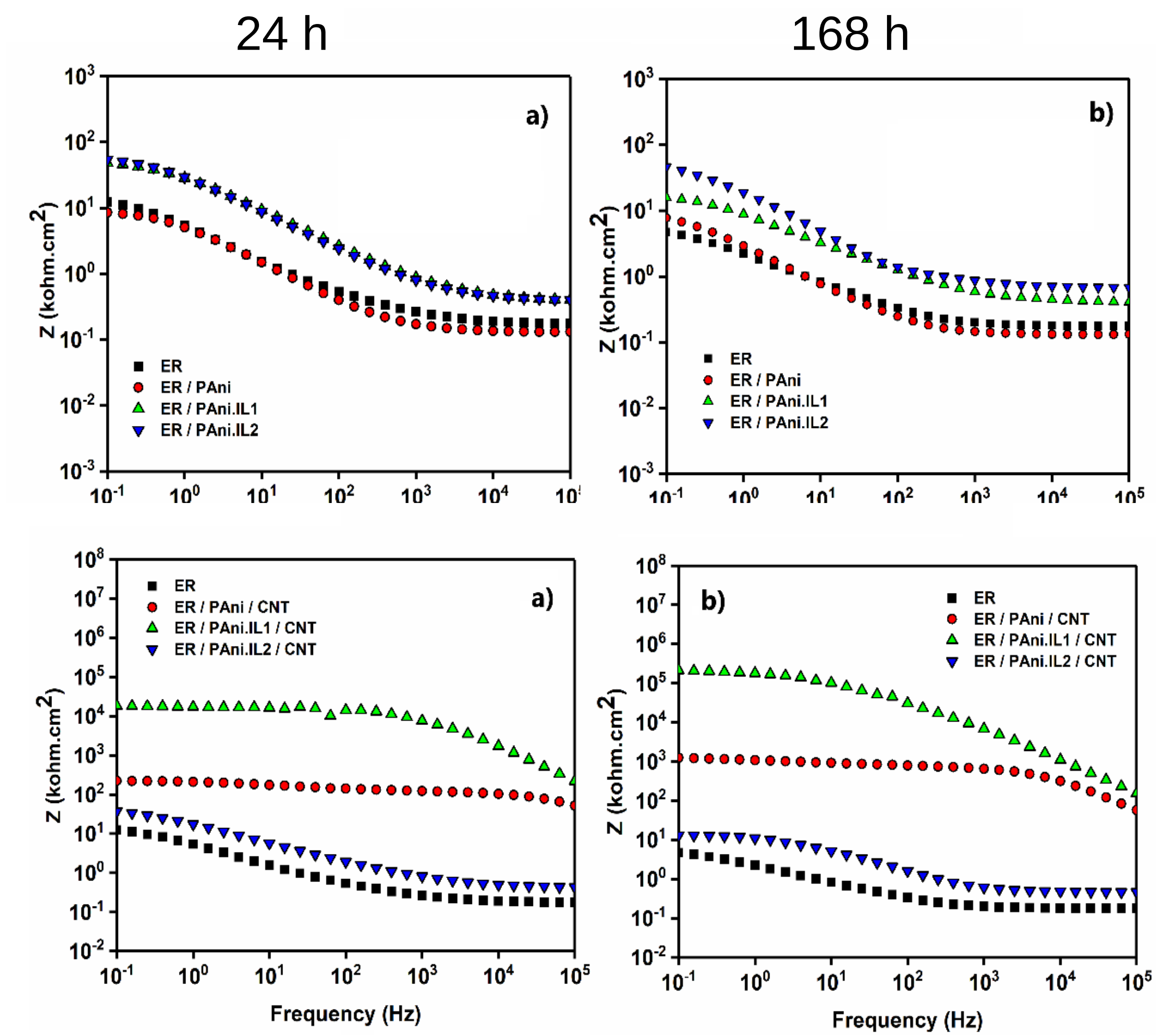
1-Methyl-imidazolium-3-butyl sulfonate (IL2)

Sample code	Ani (g)	CNT (g)	Ionic liquid nature	Ionic liquid amount (g)	CNT content (wt%)	Conductivity (S/cm)
PAni	2.7	0	-		0	1.9 ± 0.42
PAni.IL1	2.7	0	bmim.BF_4	1.35	0	2.6 ± 0.81
PAni.IL2	2.7	0	mim.butylSO_3	1.35	0	2.47 ± 0.61
PAni/CNT	2.7	0.27	-	-	11	4.01 ± 0.60
PAni.IL1/CNT	2.7	0.27	bmim.BF_4	1.35	12	4.26 ± 0.46
PAni.IL2/CNT	2.7	0.27	mim.butylSO_3^-	1.35	13	7.13 ± 0.32

Table 1. Concentration of the reagents used in the synthesis of PAni and the hybrids and conductivity
Ani = DBSA = APS = 0.03 mol; CTAB = 0.021 mol.

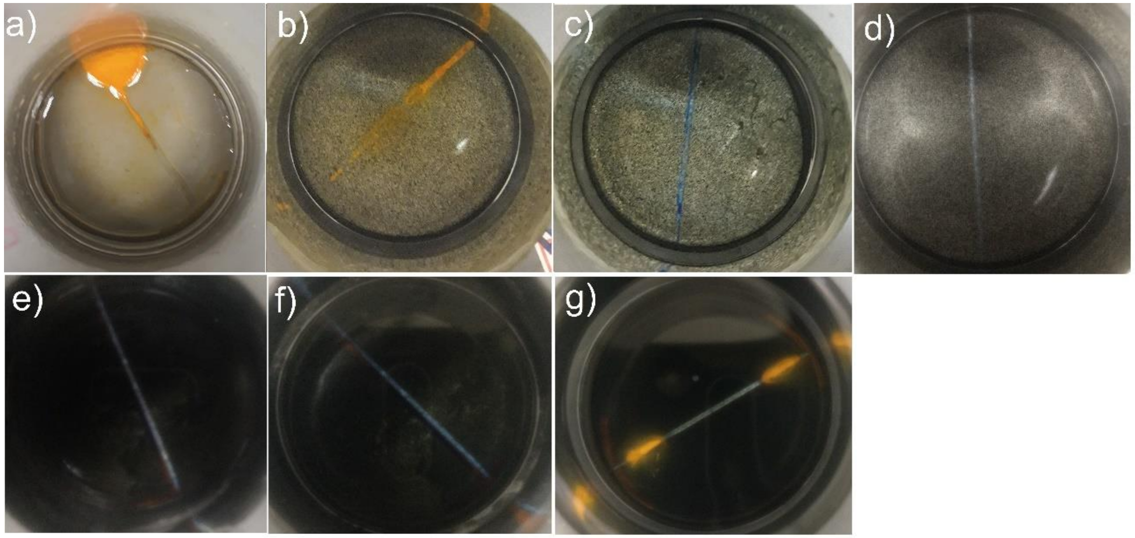
Souto et al, Prog. Organic Coatings 143, 105598 (2020)

Corrosion response of epoxy coatings loaded with 1% of Pani or Pani/CNT hybrid



Impedance of the coatings after 24 h and 168 h of immersion in NaCl solution 3.5%

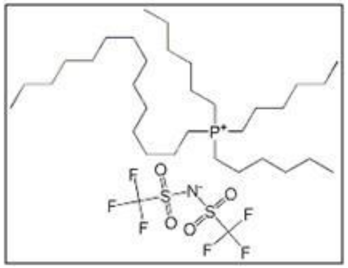
Corrosion response of epoxy coatings loaded with 1% of Pani or Pani/CNT hybrid

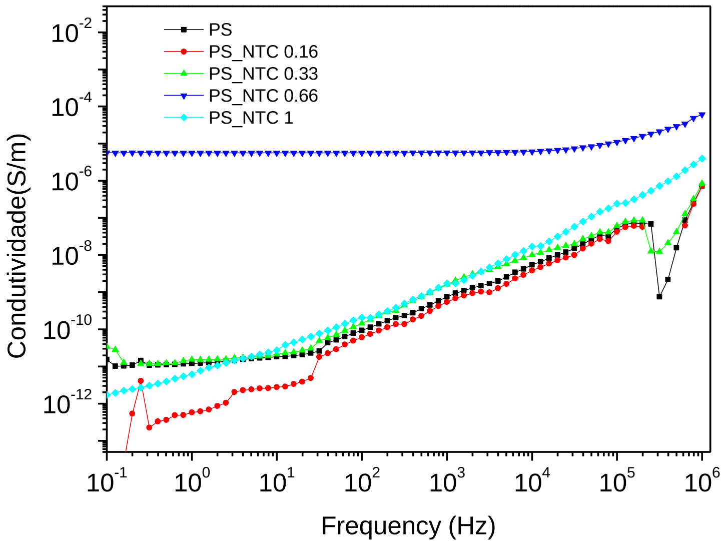


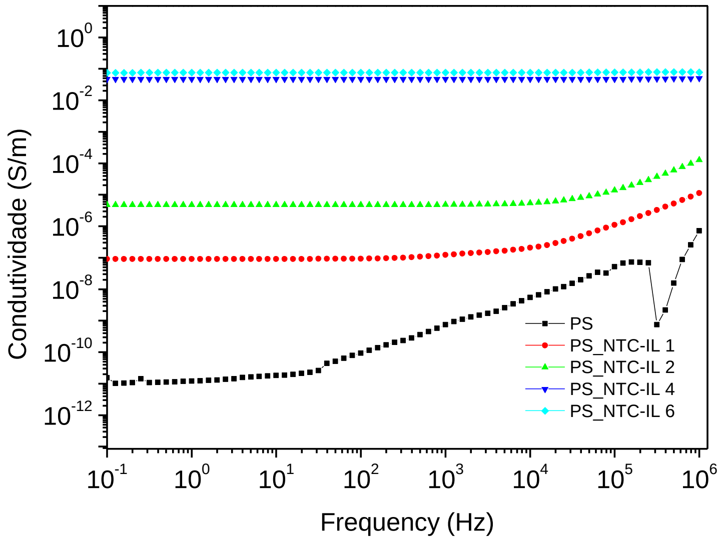
Digital photos of the (a) unloaded ER coating and ER loaded with 1 phr of (b) PAni, (c) PAni.IL1, (d) PAni.IL2, (e) PAni.CNT, (f) PAniIL1/CNT and (g) PAni.IL2/CNT after 168 h exposure into NaCl solution.

Souto et al, Prog. Organic Coatings 143, 105598 (2020)

Nanocomposites involving polystyrene and CNT







Soares da Silva et al, Mater. Chem. Phys. 189, 162 (2017)

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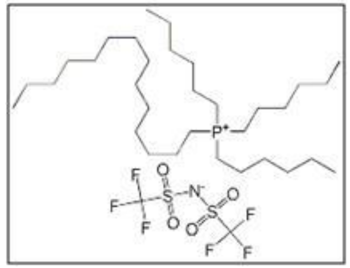
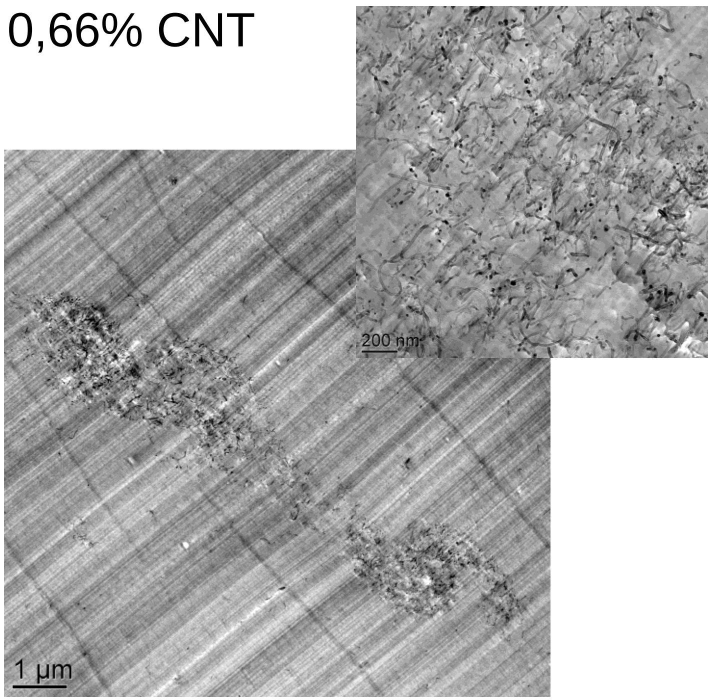
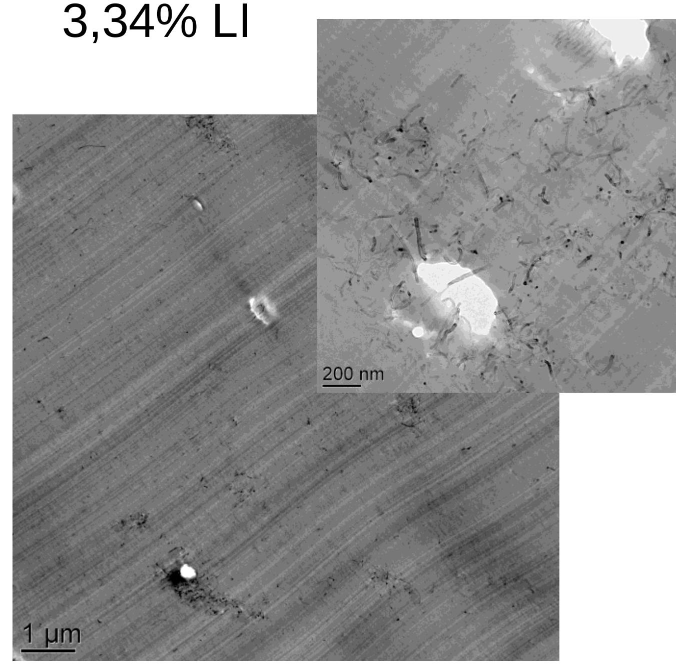


0,66% CNT



0,66% CNT
3,34% LI

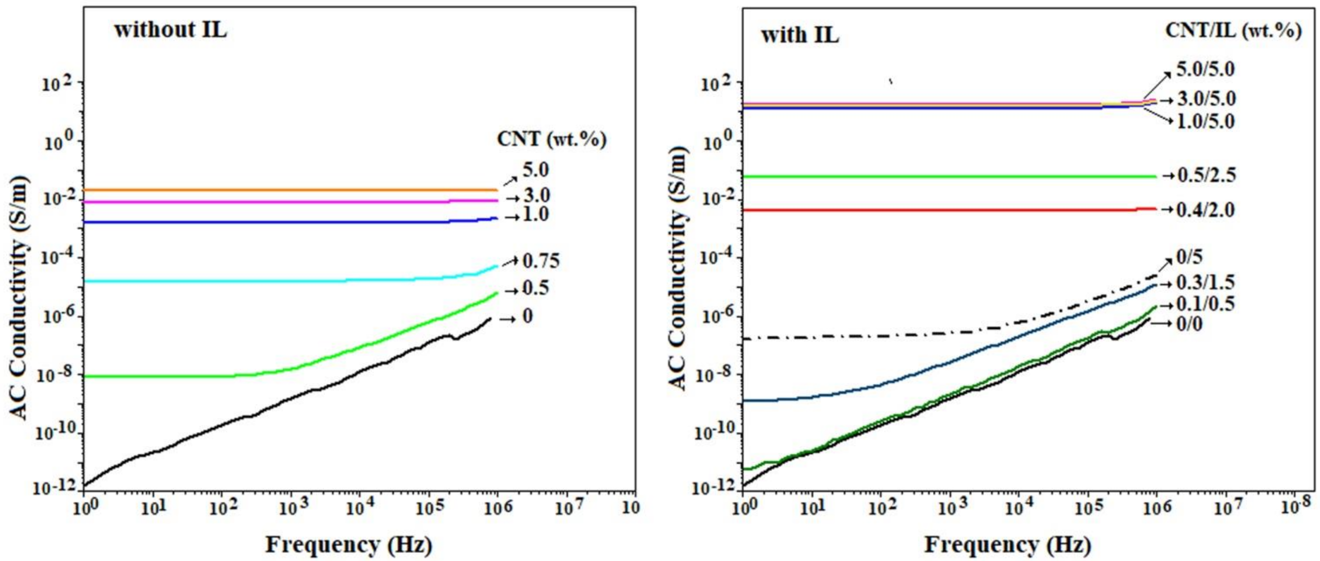


$5,7 \times 10^{-6}$ S/cm

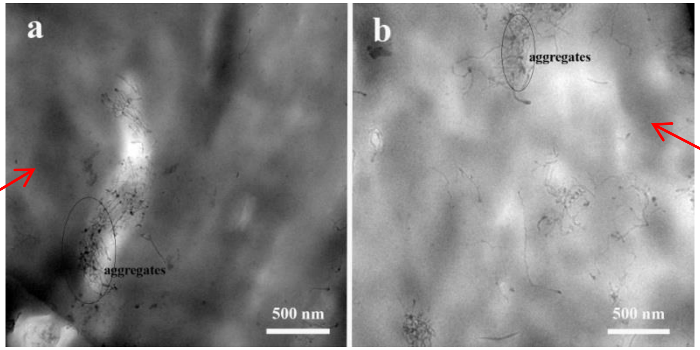
$4,8 \times 10^{-2}$ S/cm

Soares da Silva et al, Mater. Chem. Phys. 189, 162 (2017)

Nanocomposites involving PLA/PP blends loaded with CNT



1% CNT



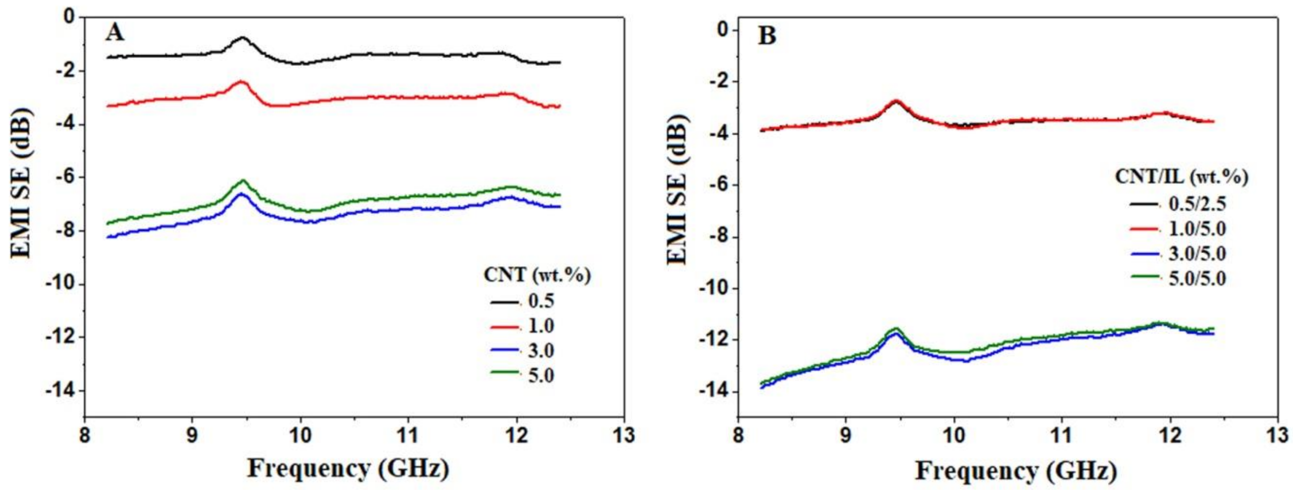
without IL
2 x 10^{-3} S/m

with IL
10 S/m

Soares et al, Polym Composites 41, 82 (2020)

Nanocomposites involving PLA/PP blends loaded with CNT

Electromagnetic interference shielding effectiveness (EMI SE)



Soares et al, Polym Composites 41, 82 (2020)

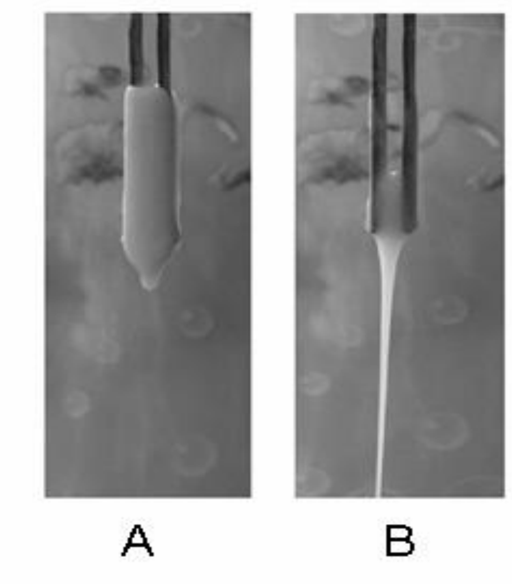
Preparation of organic modified silica and other nanoparticles

Applications in electro-rheological fluids

ELECTRO-RHEOLOGICAL FLUIDS

Electro-rheological fluids are coloidal suspensions of polarizable nanoparticles in a insulating oil.

Under the action of an electric field, the particles align in the direction of the electric field. The dipoles induced by the field cause these particles to attract each other forming fiber-like structures , which is responsible for a significant increase in the viscosity.



ELECTRO-RHEOLOGICAL FLUIDS - APPLICATIONS

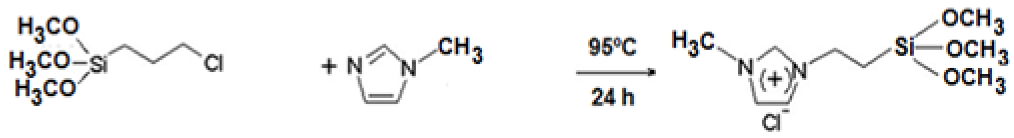
: (Ssslab, 2010)

- Automóveis: amortecedores, embreagem;
- Fluidos selantes
- Robótica
- Desenvolvimento de membros mecânicos, etc

Ref: http://www.technovelgy.com

The presence of ionic liquid in silica particles provides an increase in polarizability of the silica particles giving rise to a better electro-rheological response.

Preparation of ORMOSIL carrying ionic liquid

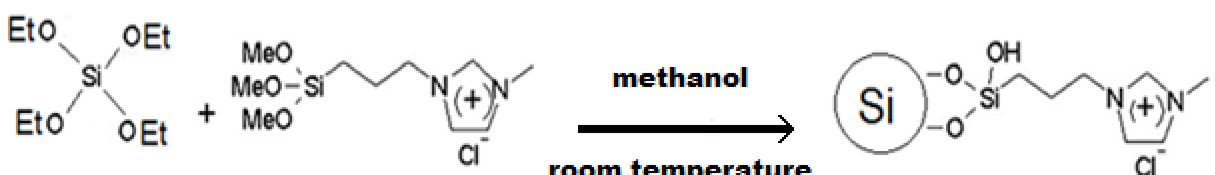


(3-chloropropyl)-trimethoxysilane

1-methyl-imidazol

1-methyl-3-(3-trimethoxysilylpropyl)-imidazolium chloride

MTMSPI]$^{+}$ [Cl]$^{-}$



TEOS

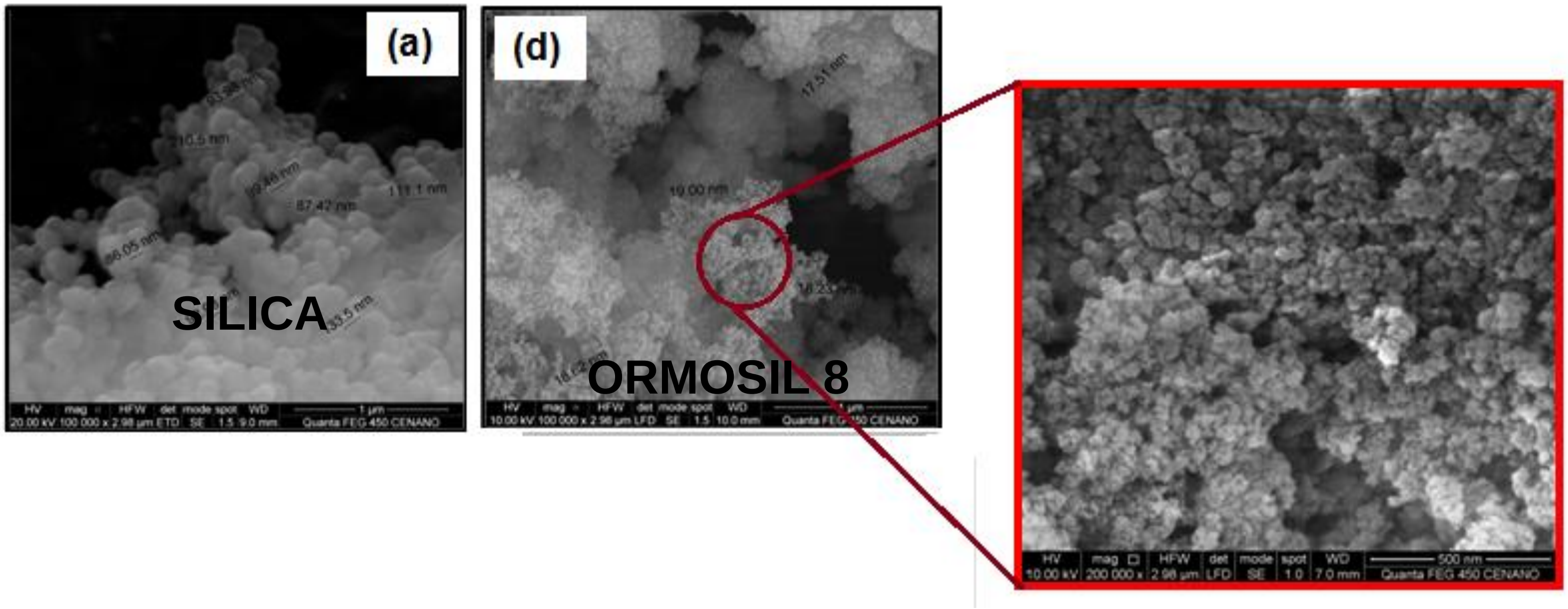
[MTMSPI]$^{+}$ [Cl]$^{-}$

ORMOSIL

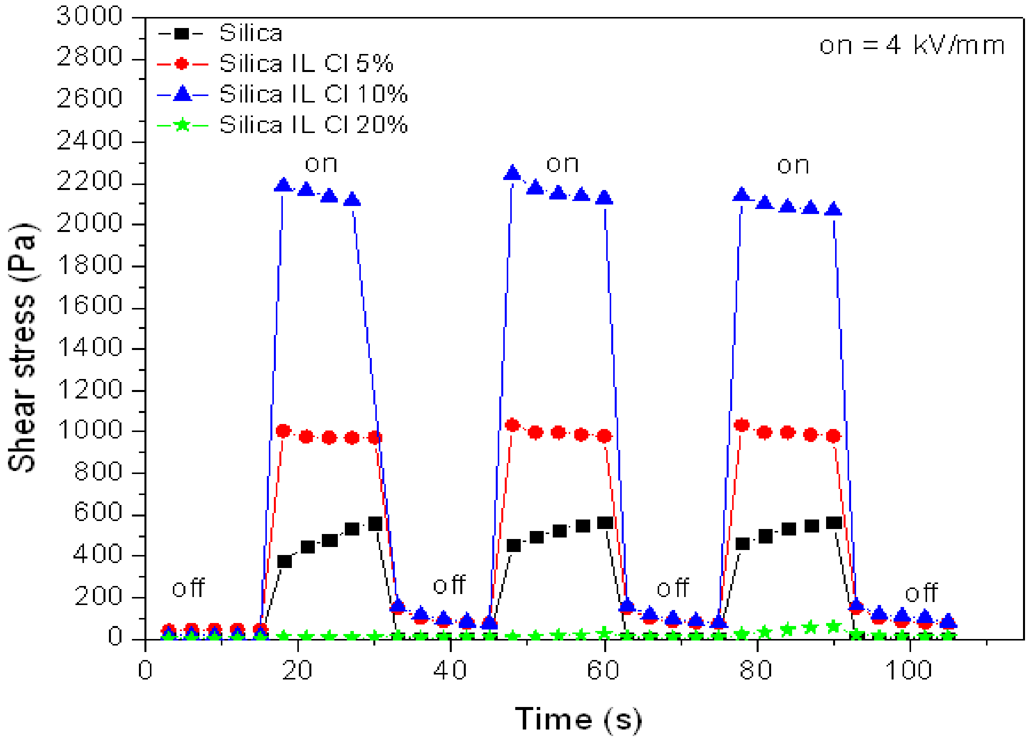
Sol gel reaction

H_2O / CH_3OH / NH_4OH
TEOS/[MTMSPI][Cl]

Morphology of ORMOSIL modified wih ionic liquid



Preparation of electro-rheological fluids 30% of particles in silicone oil



Marins and Soares, Colloids And Surfaces A 529, 311 (2017)

CONCLUSIONS

Ionic liquids are versatile materials, able to modify several properties of different materials.

They can act as:

- Curing agent for epoxy resin, with the advantage of using low amount of hardener when compared with conventional hardeners;
- They improve the dispersion of carbon nanoyube in polymeric matrices, thus resulting in an increase in electrical conductivity;
- They also contribute for an improvement of corrosion resistance of Pani and Pani/CNT – based coatings;
- Silica particles bearing ionic liquid present good electro-rheological response.

Conclusions

Another important applications of ionic liquids

- As catalysts for transesterification reactions to be used on the production of bio-based fuel;
- Ionic liquid attached on silica and other particles as magnetite, titania for adsorption of heavy metals and other pollullants;
- Preparation of solid electrolytes for batteries and other devices;

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Acknowledgements

UFRJ

CLAQ 2022 CBQ

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

FAPERJ


Ria Slides
Thank You very much