Capillary breakup and electrospinning of PA6 solutions containing $FeCl_3$: experimental findings and correlations

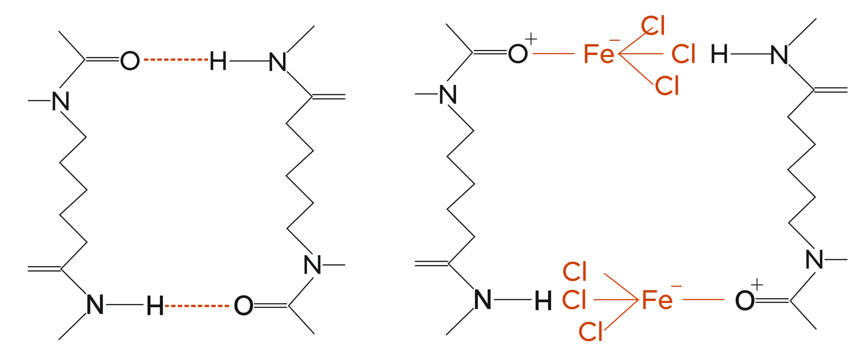
S. Formenti, R. Castagna, F. Briatico-Vangosa, C. Bertarelli

Politecnico di Milano, Dipartimento di Chimica Materiali e Ingegneria Chimica “G. Natta”

One of the main issues in the electrospinning technology concerns the control of the resulting fibres morphology. The extensional rheological behaviour of the fluid plays a fundamental role to this respect: a high degree of elasticity of the polymer solutions limits or prevents instabilities and subsequent formation of non-uniform structures [1].

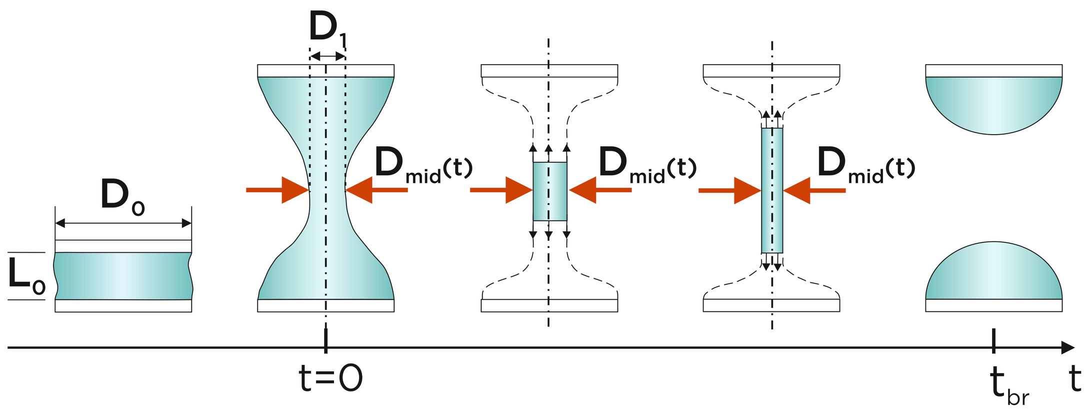
We present the case of solutions of PA6 and iron(III) chloride hexahydrate ($FeCl_3$) in formic acid, selected to electrospun a template for the following in situ polymerization of pyrrole vapours. The presence of ionic salt, essential for pyrrole growth, may disturb or even prevent H-bonds formation between amide groups of PA6 backbones, and thus perturb solution viscoelasticity.

To identify the effect of $FeCl_3$ on the system rheological behaviour and spinnability, a systematic characterization was carried out at fixed PA6 concentration (15% wt/wt) and varying the salt content, aimed at correlating electrospun fiber morphology and the extensional rheological behaviour of the solutions.



EXTENSIONAL RHEOLOGY

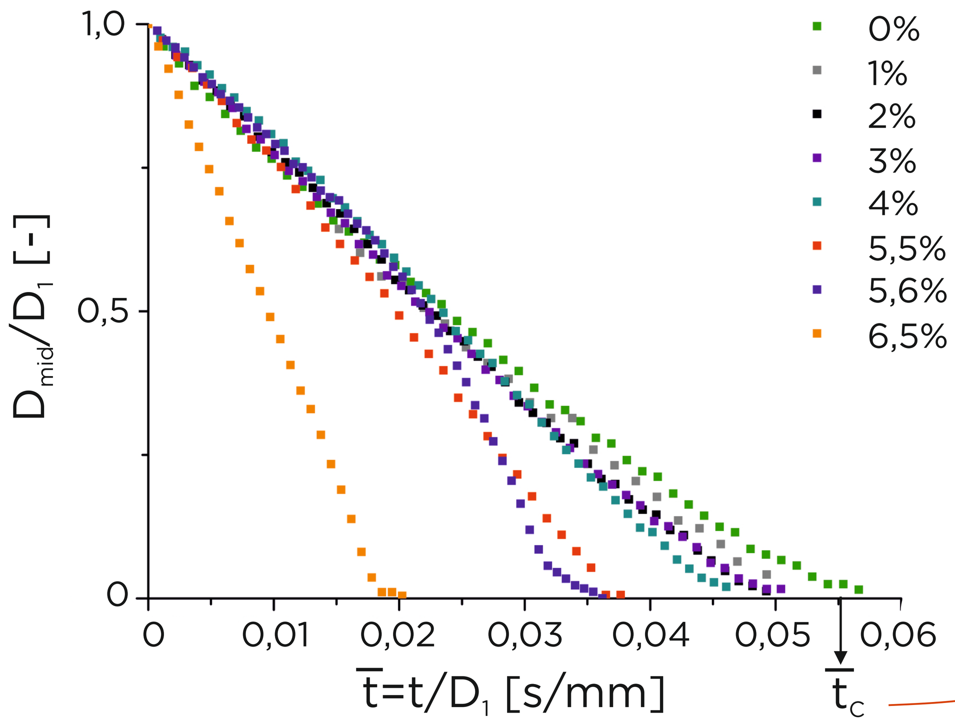
Capillary Breakup Extensional Rheometry - CaBER [2]

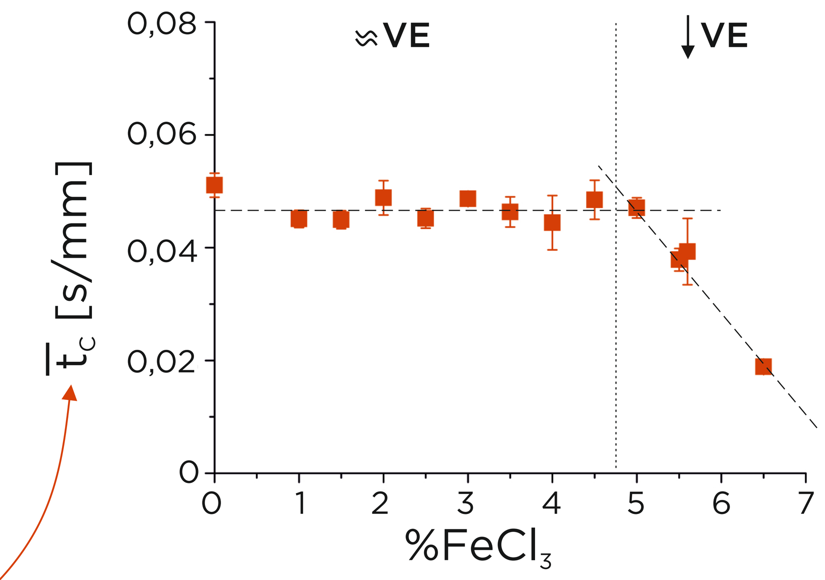


Assumptions: viscoelastic extensional behaviour

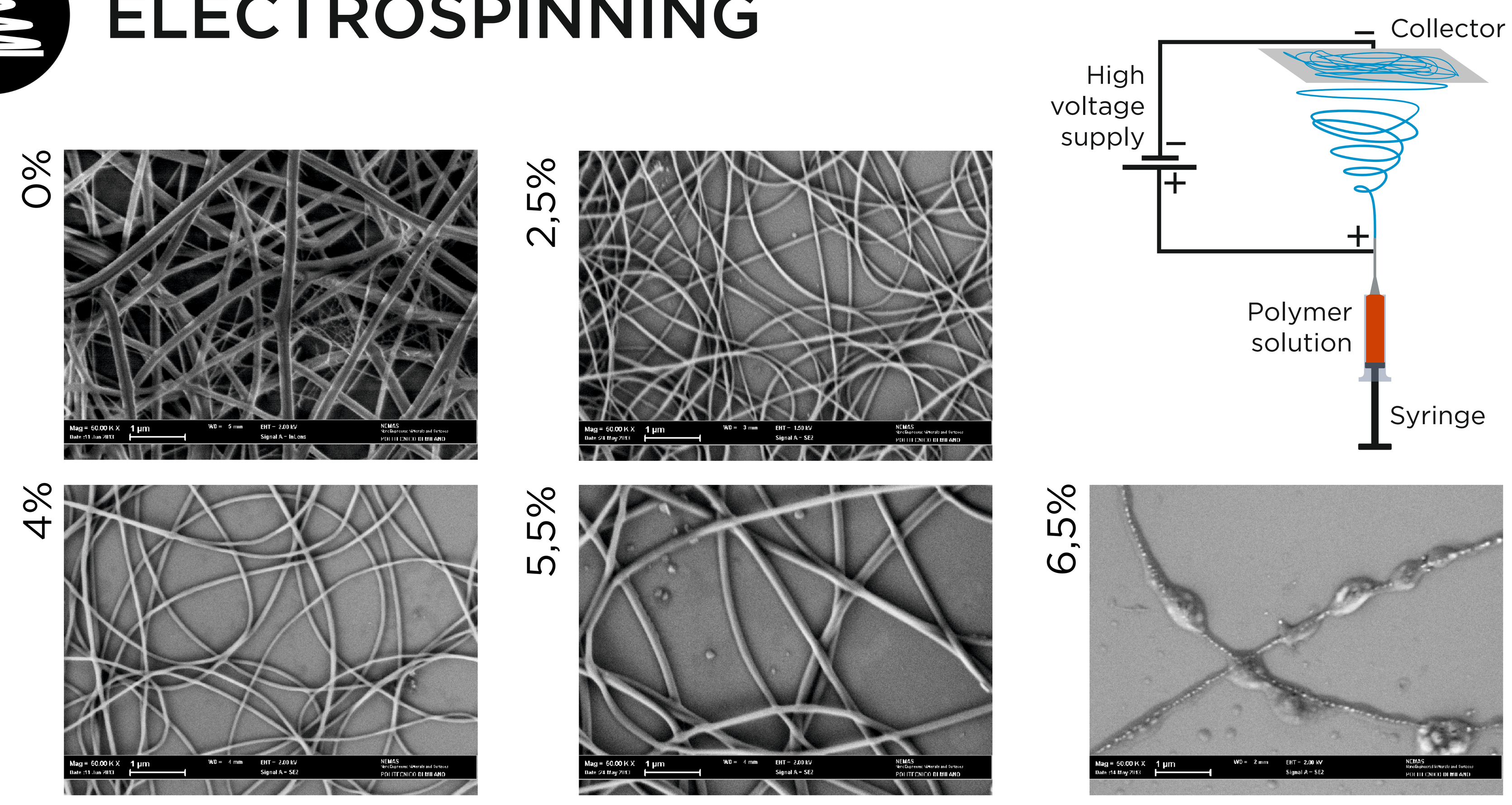
Data fitted with Entov-Hinch [3]:

$$D_{mid}(t)=D_1\left(\frac{D_1 G}{4\sigma}\right)^{1/3}\exp\left(-\frac{t}{3\lambda_c}\right)$$

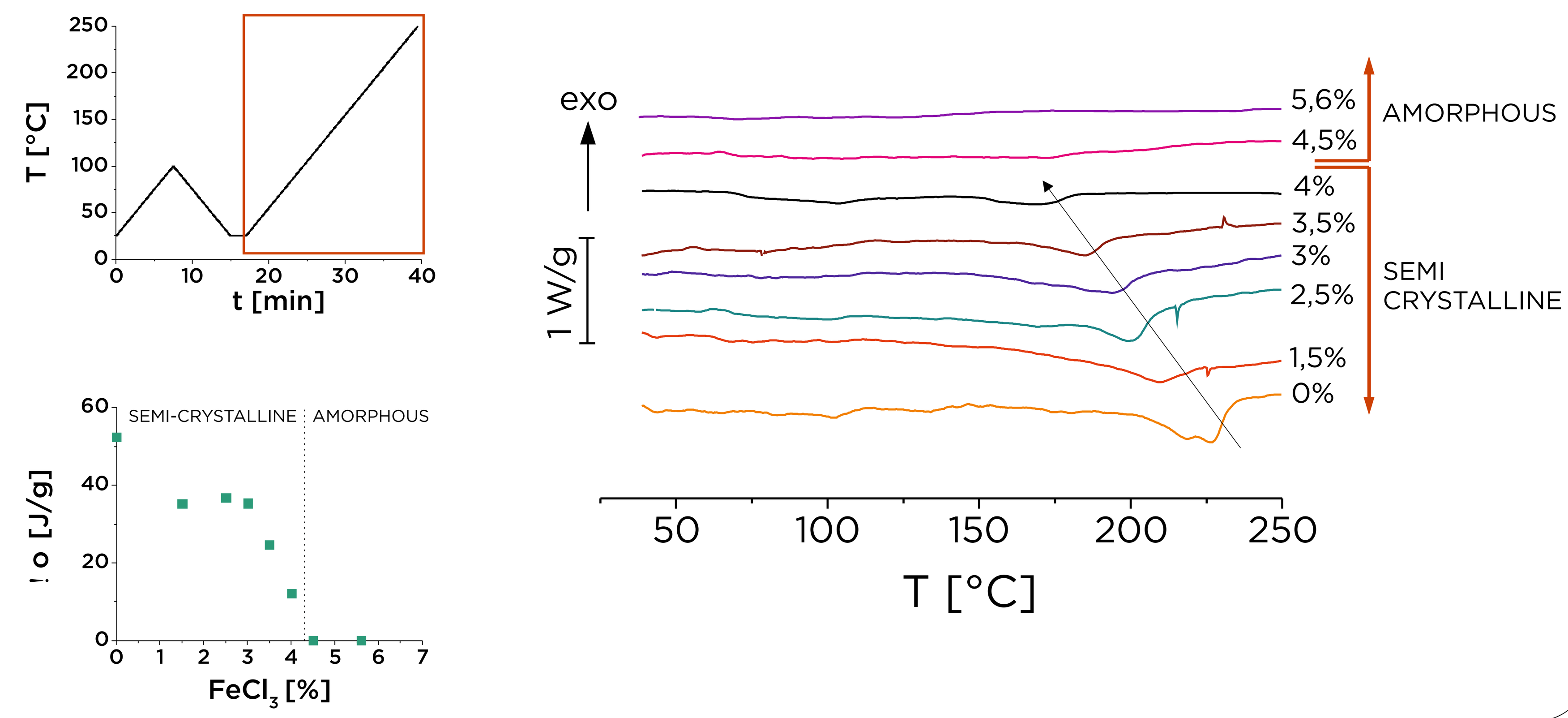




ELECTROSPINNING

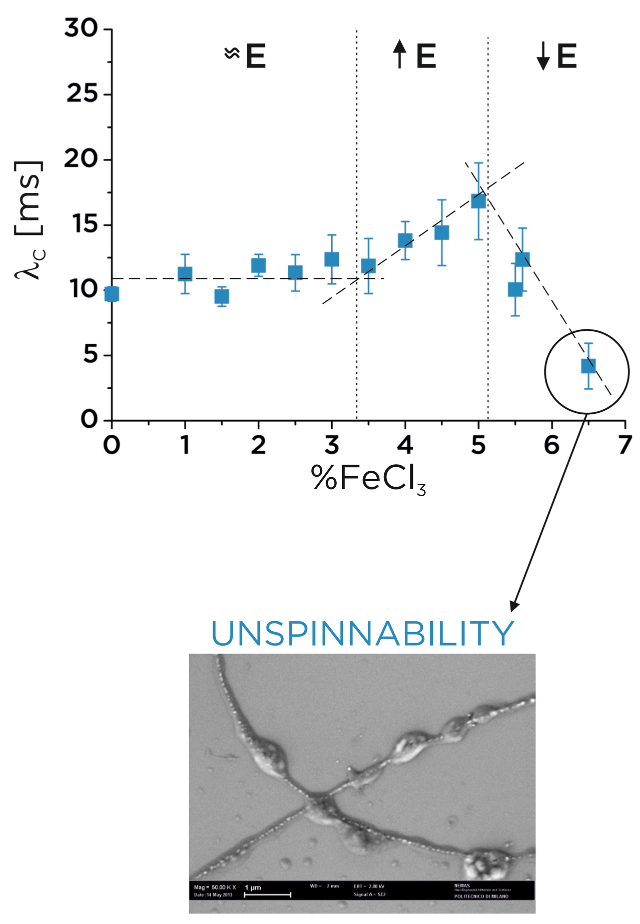


CRYSTALLINITY

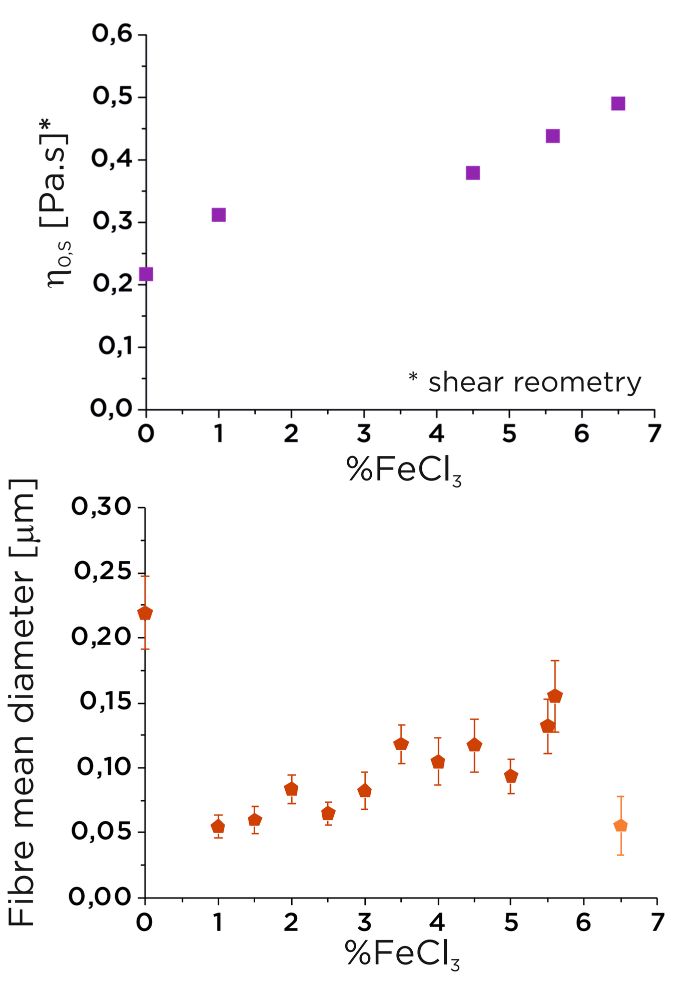


DISCUSSION AND CORRELATIONS

Effect of H-bond scission



Effect of chain solvatation

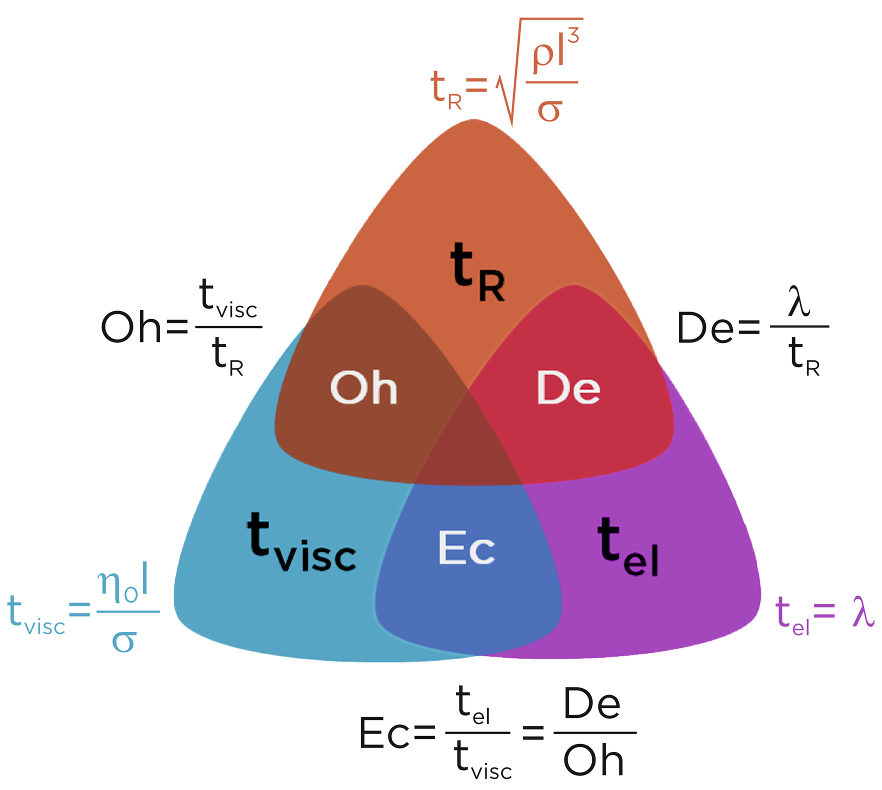


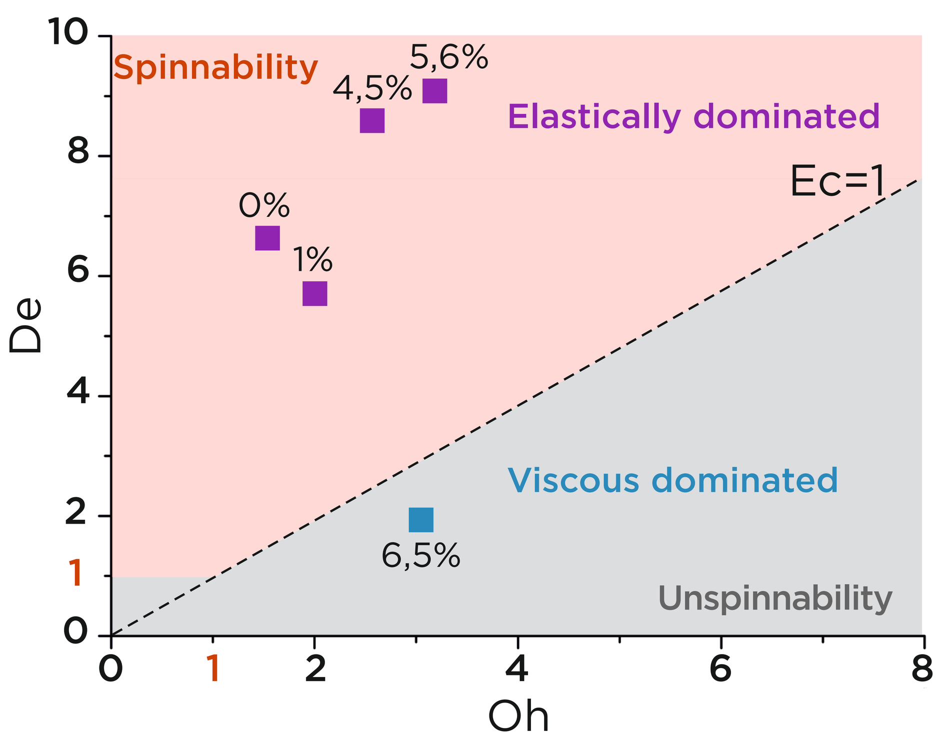
ADIMENSIONAL ANALISYS [4]

Free surface flow

‘Self-controlled thinning’

Governed by: characteristic time scales





COMMENTS AND CONCLUSIONS

The addition of the ionic salt to PA6 solutions:

- increases the shear viscosity, likely due to the swelling of macromolecular coils because of $FeCl_3$ steric hindrance;
- lowers solution elasticity due to hydrogen bond scission, induced by the formation of complexes between the salt and the amide groups of PA6 backbones.

Morphology of electrospun fibres becomes significantly inhomogeneous in correspondence to the solution characterized by Ec<1, confirming the importance of elasticity in jet stabilization. All other solutions with De>>1 (here De>6) give rise to the formation of uniform structures.

Steric hindrance of $FeCl_3$ also causes fibres to be completely amorphous above a critical concentration.

REFERENCES

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[2] G.H. McKinley, A. Tripathi, J. Rheol., vol. 44, n. 3, pp. 653-670, 2000.

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[4] G.H. McKinley, Soc. Rheol. Bulletin, vol. July, pp. 6-9, 2005.