Proposal research subject:

Rheology and processing of smart innovative Multi- Nanolayered films with controlled interfaces and tailored physical properties

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The multi-layered polymers (i.e., several polymer melts mechanically assembled via, for example, coextrusion) are attracting increasing attention due to their promising applications in the fields of nanotechnology, nonlinear optics and microelectronics, etc. Presently, micro- and nano-layer films with high quality are able to be produced via the newly developed layer multiplying coextrusion or so-called forced assembly layer coextrusion (FALMCO, which enables the fabrication of large-scale biaxially oriented films with thousands of alternating layers. However, a major drawback of this actual process is that the different melted polymers need to have similar viscoelastic properties. The bi-stretching step with high cost is also required to reduce more the layered thickness. The FALMCO process has the same kind of benefits and drawbacks, but it allows to strongly decreasing layers' thickness simply by changing the film volume composition, the film thickness, and/or the number of layers. The resulting multiscale architectures built from the Nano- to the micro level thus enables new and attractive properties worth to be more deeply studied. But the scaling effect obtained with the current multiplier dies used in FALMCO also generates large stress and pressure drops in the die due to the large cross section reduction and to the flow asymmetry during the compression-then-expansion step. Viscous encapsulation, i.e. thickness non-uniformities can occur. Interfacially driven layer instability and break-up of the thin layers may also result during layer multiplication if polymers streams possess a relatively large rheological mismatch. Moreover, the total residence time in the die is still too long for highly thermally sensitive polymers leading to potential degradation. Many interesting researches on this topic (especially in CWRU-USA, Sichuan U.-China) have focused only on the characterization of the final films' properties and especially their microstructures. In such conditions, the interfacial properties in solid and melt are far from being enough well understood to optimize the process and customise films' properties.

The present thesis deals with the Multi-scale Studies of Bulk and Confined Multi- Nanolayered Structures based on model polymers with tailored interface/interphases properties. The obtained systems are dedicated to be used as capacitors and for storage energy. Main objectives of the present thesis are to understand the fundamentals of the interfacial phenomena (interfacial reaction, interdiffusion, interfacial slippage as well crystallization kinetics) over different length scales (from macro- to micro- and Nano-sizes). With a goal to know the effect of confinement on the interfacial phenomena, this thesis will deal with physico-chemical affinities (i.e. interphase) at bulk reactive/nonreactive interfaces (macro-scale) by coextrusion and at confined diffuse or reactive interfaces (micro-, nano-scale) by layer-multiplying coextrusion.

The first part of the present thesis will focus on the better chose and characterizations of compatible polymer pairs as well PVDF or its copolymers to be confined by PMMA or PC with various molar masses [SC/amorphous]. Other systems based on filled PVDF layers will be studied in coupling with other dielectric polyamide. A deep understanding of the effects of functionalization, molar mass, and polydispersity on the structural and rheological properties will be performed. Through rheological study in both shear and elongation, melt dielectric properties experiments and modelling we will attempt to understand and tune the properties of the developed interfaces/interphases. The performance of the interface/interphase triggered between these polymers is closely related to the interfacial structure, exactly speaking, local entanglements that are gradually established from diffusion and/or reaction. The reactive interface/interphase includes a complete, By virtue of layer-multiplying coextrusion technology, the interfacial area and the amount of interphase could be greatly amplified. It will be exciting task to investigate hierarchical sequence of multi-scale phenomena spanning from nano-scale in term of segmental motions, micro-scale of interfacial tension reduction and morphology evolution to macroscopic scale of mechanical/rheological modifications

Secondly, effects of the triggered interface/interphases in multi micro-/nano-layered polymer crystalline and architectural structures will be studied. Effects of the contact time (ie. given for diffusion or reaction), temperature and viscoelastic mismatch will be investigated in term of flow stability and layer homogeneity. By means of rheology and dielectric spectroscopy, the influence of geometrical and macromolecular confinement on interfacial dynamics,

and rheology of multi-layered polymer systems will be examined. Layer homogeneity and morphological properties will be studied in turn by AFM, TEM. The developed crystalline properties in Nano layered structures will be in turn evaluated by WAXS and SAXS. The changes in solid dielectric properties resulting from layer multiplication will be evaluated depending of the developed interphases and crystalline morphology. .
Overall, based on the understandings of the fundamentals of the interfacial phenomena over multi-scales, the outcome of the thesis should foster development of new coextruded multi-, micro- and nano-layer films with tailored transport, dielectric or ferroelectric properties with tuned optical and gradient properties.

International collaboration: Pr. Joao Maia from the group of Pr. Eric Baer Case Western Reserve University-(CWRU) (CLIPS- CWRU-USA). Also with Dr. Bo Lu, a previous Phd Student of our group.

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Authors' quoted references in the field:

[1] B. Lu, K. Lamnawar, A. Maazouz 2017, *Rheological and dynamic insights into the in situ reactive interphase with graft copolymer in bilayered system.* **Soft Matter** 2017, 13, 2523 – 2535

[2] B. Lu, K. Lamnawar, A. Maazouz. 2016. *Revealing the dynamic heterogeneity of PMMA/PVDF blends: from microscopic dynamics to macroscopic properties.* **Soft Matter**, 2016, 12, 3252-3264.

[3] H-G Zhang, K. Lamnawar, A. Maazouz and J. M. Maia. 2016 *A nonlinear shear and elongation rheological study of interfacial failure in compatible bilayer systems.* **Journal of Rheology** 60, 1-23

[4] H-G Zhang, K.Lamnawar, A. Maazouz J. Maia 2015 *Experimental considerations on the step shear strain in polymer melts: sources of error and windows of confidence.* ***Rheologica Acta****, 54:121-138, 2015*

[5] H-G *Zhang*, Lamnawar K., Maazouz A. 2015. *Fundamental Understanding and Modeling of Diffuse Interphase Properties and its Role in Interfacial Flow Stability of Multilayer Polymers.* **Polymer Engineering and Science**, 55(4):771-791. doi: 10.1002/pen.23945

[6] A. Bondon, K. Lamnawar, A. Maazouz. 2015. *Experimental Investigation of a New Type of Interfacial Instability in a Reactive Coextrusion Process* **Polymer Engineering and Science**, 55, 2542–2552.

[7] K. Lamnawar, H. Zhang, A. Maazouz. 2013. *A State of the art on the coextrusion process: fundamental and experimental approaches,* ***Encyclopedia of Polymer Science and technology*** *(Wiley library, New York, 2013).*

[8] H-G.Zhang, K. Lamnawar, A. Maazouz, 2013. *Rheological Modeling of the Mutual Diffusion and the Interphase Development for an Asymmetrical Bilayer Based on PMMA and PVDF Model Compatible Polymers.* **Macromolecules** Volume: 46 Issue: 1 Pages: 276-299. http://dx.doi.org/10.1021/ma301620a.

Short CV of the principal supervisor:

Dr. Khalid Lamnawar's research is focused on polymer science, rheology and processing with a dual research dedicated to experimentation and modelling. The main objective is developing some multi-scale studies to link the rheology of polymers, processing technology and properties of micro/nanostructured materials together. He is the author of more than 125 references, including 50 articles in peer-reviewed journals (48 already published and referenced in Scopus or WOS), 2 Book chapters, 1 Editorial Book of Abstracts & proceedings,…., 2 patents, 70 proceedings, and more than 60 international conferences with oral presentations, many keynote and invited speaker in national or international conference, university and Industry, 24 national Conferences. He is also a reviewer for internationally reputed scientific journals…He has co-supervised and been the advisor for more then 30 Master's theses, 11 PhD of which 7 have already been defended. One of his PhD students (2010-2013) working on "Interfacial rheology of compatible multilayer structures" was awarded "The Best Doctoral Dissertation" by the French Rheology Group (GFR). He is author of some of invited & keynote lectures in the industry, universities and international conferences as well at word or regional PPS. Recently, he was the Scientific and Technical Program Coordinator, Secretary and webmaster of the 32nd international Conference of the Polymer Processing Society- France- July 25-2, 2016, 750 attendees. https://pps-32.sciencesconf.org/ (Chair: Professor A. Maazouz). His great contribution took more than 3 years for preparation and it was one of the key for the event success. He also provided some expertise for French Government and European Projects: ANR" National Research Agency', Biomedicine Agency, Ministry of Industry… Thanks to his outstanding contributions, he has been recognized with numbers of awards, including….(Excellence grant for research, 1st rank" from French government. He is member of the editorial Board of Journal of Composites and Biodegradable Polymers. Since 2017, he is head of Mechanical Engineering Plastics Processing through apprenticeship engineers department. He is author of some features paper in high impact factor journals. He also provided some expertise for French Government and European Projects: ANR" National Research Agency', Biomedicine Agency, Ministry of Industry, European Research Foundation, ACS, Some recent contributions are available at: https://www.researchgate.net/profile/Khalid_Lamnawar. The defence of his 'HDR' is scheduled by the end of December, 2018.