Congratulations go to Pouyan Sardashti, PhD 2014, Department of Chemical Engineering, who received the international and extremely prestigious 'Borealis Student Innovation Award 2014', awarded via an international competition to one PhD student per year for innovative work in the PhD thesis category. Pouyan completed his PhD thesis in the Department of Chemical Engineering. His PhD thesis title was 'Methodologies for Obtaining Reliable Indicators for the Environmental Stress Cracking Resistance of Polyethylene'. Pouyan's PhD work traversed a multidisciplinary area between polymer science, polymer engineering, polymer melt rheology and mechanical/tensile material properties, with polyethylene pipes as the final application target, and as such, he interacted very closely with Professors Alex Penlidis and Costas Tzoganakis of Chemical Engineering, and Marianna Polak of Civil Engineering at the University of Waterloo. His PhD thesis has also received support from Imperial Oil (ExxonMobil Chemical Canada), with close interactions with researchers at Imperial Oil Canada in Sarnia ON. After his PhD thesis defence in February 2014, Pouyan joined BASF Corp., USA, in March 2014.

Borealis receives every year an impressive selection of high quality work from talented students around the world for this award, so it is a distinct honour for Pouyan to be selected as the winner for 2014. Pouyan was presented with the award (and gave a seminar) at a special ceremony in Linz, Austria, in January 2015.

Environmental stress cracking (ESC) is a major problem of polyethylene (PE) products and the determination of its resistance (ESCR) is of utmost importance for resin producers, plastics processors and end-users. Principal objectives of the doctoral research were to conduct studies to identify, quantify, and improve ESCR of PE resins. Several experimental stages were conducted in relation to detailed determination of molecular properties, extensional testing both in the solid and melt states, and the effect of temperature on crystalline phase properties during processing and post-processing. Moreover, reactive extrusion techniques were employed in order to enhance (in principle) the ESCR of polyethylene via the formation of long chain branches (LCB).

ESC, the most common failure mechanism involved in polymers, occurs suddenly, without any visible pre-fracture deformation. Such failure can be catastrophic and costly; therefore, a true and reliable measure of such property is of great essence. In PE, ESC occurs through a slow crack growth (SCG) mechanism, where molecular deformation starts from existing microscopic inhomogeneities, introduced during production, processing, and installation. The molecular deformation during SCG includes craze initiation and propagation. This failure mechanism can be preceded by chemical diffusion and local plasticization of the inhomogeneities, if PE is subjected to an aggressive chemical environment. The collapse of crazes ultimately introduces a crack surface, which then joins other microscopic crack surfaces, and causes a brittle failure.

Research was conducted to design and develop practical and reproducible standard characterization techniques, for the first time in the literature, to predict and quantify polyethylene cracking resistance behavior. To develop a reliable, yet practical characterization technique, attempts were made to find relationships between molecular structure characteristics and material responses, mainly inter-lamellar entanglements and strain hardening behaviour of PE resins. This work was accomplished through mechanical and rheological experiments. Inter-

lamellar entanglements are believed to be the main factor controlling ESCR in PE. Extent of entanglements and entanglement efficiency were investigated by monitoring the strain hardening behaviour of PE resins in the solid state through a uniaxial tensile test, and in the melt state, through extensional rheometry.

Firstly, a standard tensile specimen was designed, and a uniaxial tensile test was developed for a relative evaluation of ESCR. These were developed by rigorous design of experiments and statistical analyses. Through the developed characterization technique, a factor called "corrected hardening stiffness (cHS)" was developed, which can easily be used for a relative ranking of ESCR of PE resins with different molecular and structural properties. The developed test offers a more reliable and consistent ESCR picture without the drawbacks of the conventional characterization techniques (i.e., subjective notching process, presence of aggressive fluids). In addition, a reliable standard correlation was established between ESCR and cHS, which ultimately allows for a practical estimation of resistance to fracture, in units of time. This correlation was constructed based on a broad spectrum of linear low density PE (LLDPE), high density PE (HDPE), and pipe grade polyethylene resins. While many accepted techniques have a degree of subjectivity, cHS seems to be general, universally applicable and reliable in ranking or selection of resins.

Secondly, studies were extended to the melt state via shear and extensional rheometry. Through studies in the shear mode, a molecular weight-normalized average characteristic relaxation time was found to be efficient in predicting the extent of chain entanglements in resins. This provided a potential melt indicator for a relative measure of ESCR. Through extensional measurements, an inverse correlation was obtained between ESCR and the melt strain hardening coefficient (MSHC), found from Sentmanat Extensional Rheometry (SER). This indicated an inverse relationship between ESCR and chain extensibility in the melt. In addition, a new factor called "melt hardening stiffness (mHS)" was developed, for the first time in the literature, from the slope of a stress-strain line, obtained from SER. This factor, analogous to cHS, can be used for a practical and reliable ranking of ESCR of PEs.

ESCR is usually associated with classical crystalline phase property indicators, such as crystallinity, lamella thickness and lamella area. In the third stage of this study, the effects of processing and post-processing temperature on the extent of inter-lamellar entanglements were investigated, evaluated, and correlated to ESCR. Analysis of the lamella surface area (LSA) was pursued since LSA reflects changes in phase interconnectivity more precisely. The focus of this part of the study was on the effect of temperature on LSA to identify the optimum processing and post-processing conditions which yield a higher LSA. It was reasonable to presume that PEs with larger lamella lateral surface areas will have more inter-lamellar entanglements, hence higher ESCR. In addition, multiple correlations were developed to address the ambiguity in the literature between ESCR, crystallinity, lamella thickness and lamella lateral area.

Finally, a well-controlled ultraviolet (UV) photoinitiated reactive extrusion (REX) process was developed for selective formation of long chain branches in the PE structure. This was conducted to impose restrictions against stretching of the polymer chain, which consequently enhanced ESCR. This modification, yielding a remarkable fourfold increase in ESCR, was achieved with minimum polymer degradation or crosslinking.

Ultimately, the PhD thesis has suggested a set of prescriptions that relate micro-molecular chain indicators (defined in the reactor during production) with mechanical/tensile properties of PE, ESCR being one of them (governed by post-processing steps). The target was to relate a very empirical and unreliable indicator (ESCR), with a more fundamental property (hardening stiffness, from a stress-strain test), which is more precise and reliable. As such, it is possible in the near future to replace a test, currently in use as a standard (via ASTM or ISO) for the last 20-25 years, with another test that will be more reliable, with less variability, and independent of the specific material.

The figures that follow offer a quick overview of Pouyan's PhD work. Figure 1 gives a sample of Pouyan's mechanical and rheological testing that led to the suggestion of new indicators for evaluating ESCR of different polyethylene resins. Figure 2 shows an example of different property 'maps', relating important polyethylene properties such as density, molecular weight, crystallinity and ESCR. These maps would allow one to select the appropriate polyethylene resins for a specific performance target. More information and details can of course be found in Pouyan's PhD thesis and publications.

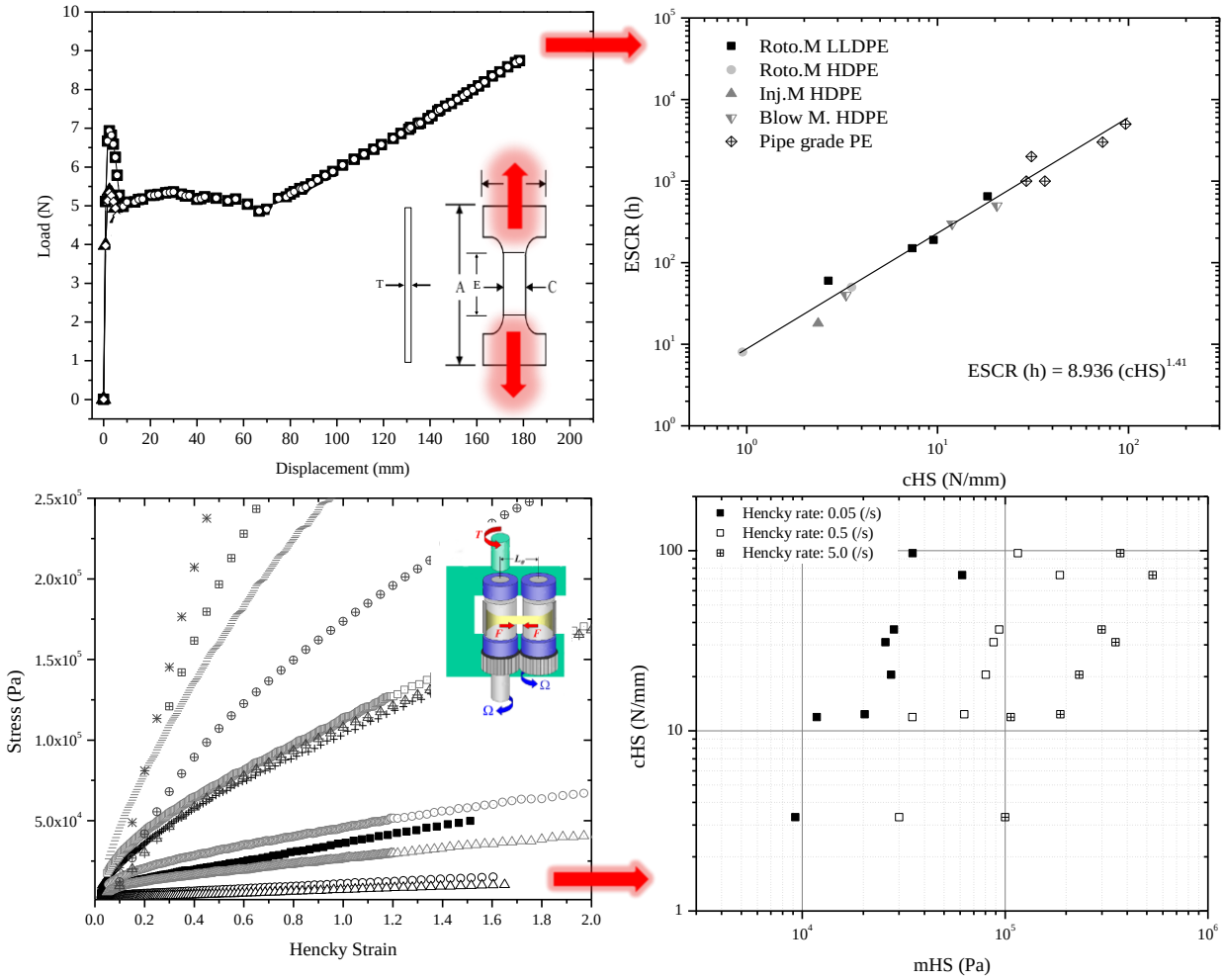

Figure 1: Mechanical (tensile strain hardening test) and rheological (Sentmanat extensional rheometry) testing used in this work to identify reliable indicators of ESCR of polyethylene

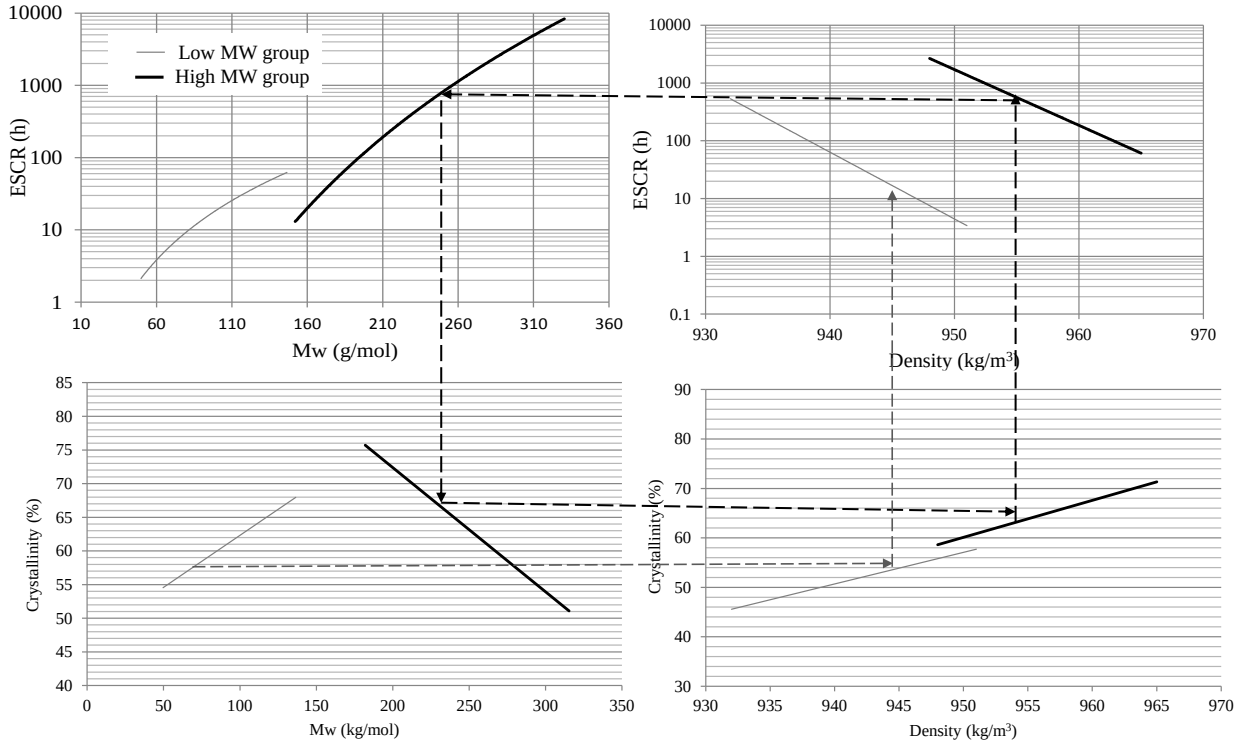

Figure 2: Property maps developed to relate ESCR with main structural properties of a large variety of polyethylene resins