Full Paper

Operational Maps Between Molecular Properties and Environmental Stress Cracking Resistance (ESCR)

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Abstract. Environmental stress cracking (ESC) is one of the main failure mechanisms involved in polymer fractures. This paper focusses on the environmental stress cracking resistance (ESCR) of polyethylene (PE) in which ESC occurs through a slow crack growth mechanism. In order to predict the ESCR of PE, it is necessary to fully understand the molecular structure of the resin. This paper demonstrates the relationships between molecular structure characteristics and material responses based on experimental characterization and published literature trends. Relationships between ESCR, molecular weight (MW), percentage

crystallinity, and density were used to create ESCR and molecular structure maps, which can be used to improve the development of PE resins with a desirable (better/higher) ESCR. These maps along with a logical flow chart offer practical prescriptions and describe pathways towards the development of PE with a desirable ESCR. In addition, this paper presents case studies that demonstrate the effectiveness of this approach.
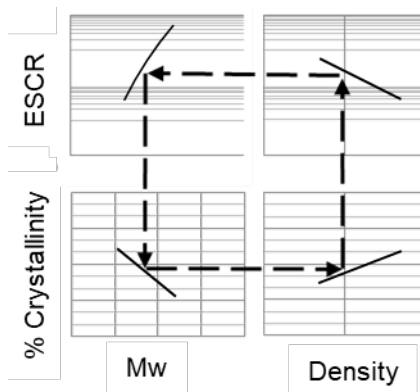
1. Introduction

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. The principal objectives of prior recent research[1] were to conduct experimental 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 of PE resins. 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 a failure can be catastrophic and costly; therefore, a representative and reliable measure of ESC is of great importance. 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 brittle failure.[2-9]

The research was conducted in four stages in order to design and develop practical and reproducible standard characterization techniques for predicting and quantifying 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.[3,6] 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.[1,2]

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 arrived at, which can easily be used for a relative ranking of ESCR of PE resins with different molecular and structural properties.

The cHS was found in two stages. The first stage included performing tensile tests according to a newly designed test specimen and uniaxial tensile test. The measured slope from the strain hardening section of the test was called the "hardening stiffness (HS)", which had shown to be a strong indicator of ESCR of similar grades of PE. The second stage included developing a "correction factor" to emphasise the effect of subtle molecular chain differences (short chain branches) on ESCR of different grades of PE. 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 (see Figure 1), 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 polyethylene resins with different MW and branching types and content, including, 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.[4,10]
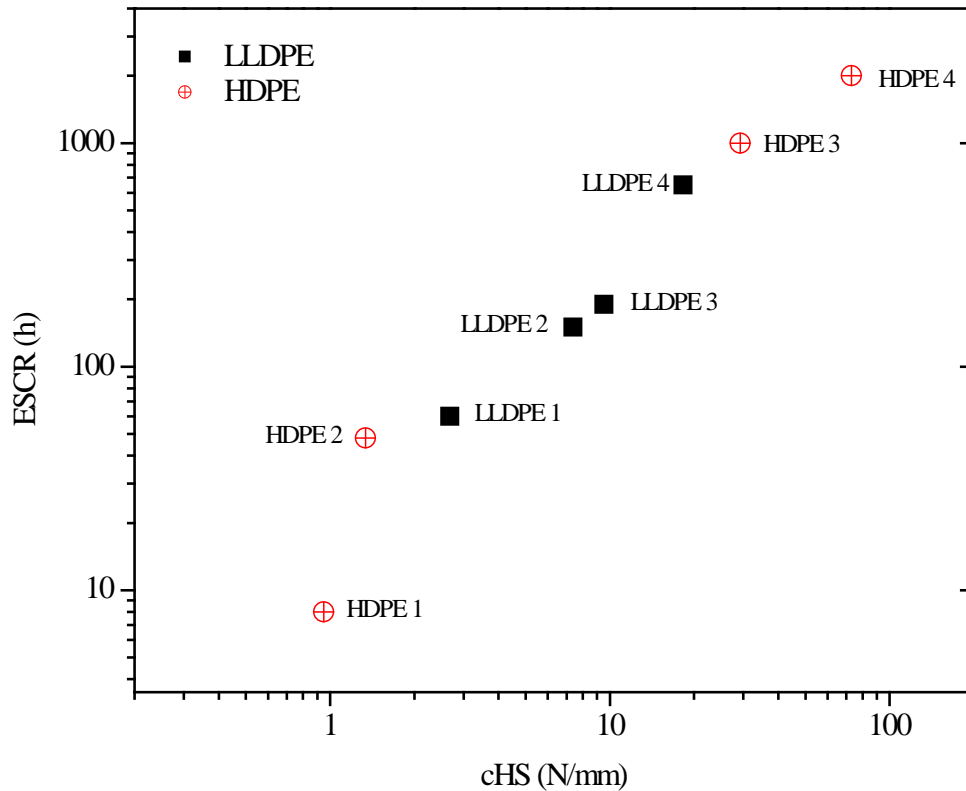
Figure 1. ESCR vs cHS graph of different types of PE resins. Table 1 summarizes molecular properties of these PE resins.

Secondly, studies were extended to the melt state via shear and extensional rheometry [1-2]. The objective was to identify potential melt properties that are affected by the polymer molecular structure; namely, short and long chain branches (content and length), which control the extent of chain entanglements and ESCR. It is well accepted that presence of side chain branches improves the long-term mechanical properties of PE resins [7, 11-13]. 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 above, can be used for a practical and reliable ranking of ESCR of PEs.[2]

The mHS, is a melt state factor that reflects the polymer molecular chain structure. This factor was found to be sensitive to polymer properties that have a direct influence on ESCR, namely MWD or type and extent of branching, that are not easily predicted by the solid state conventional ESCR characterization techniques [9-10, 14-15]. Similar to the cHS, mHS is determined from the strain hardening portion of a stress-strain curve under uniaxial tensile deformation; however, the test is conducted in the melt state through an extensional rheometry (SER). A direct correlation between mHS and cHS was expected as both factors are fundamentally controlled by polymer molecular properties affecting ESCR. This correlation is shown in Figure 2, where both types of measurements (solid (cHS) vs. melt hardening stiffness (mHS) tests) indicated the same trend. This observation verified the potential of using either of the strain hardening indicators for the estimation of ESCR.
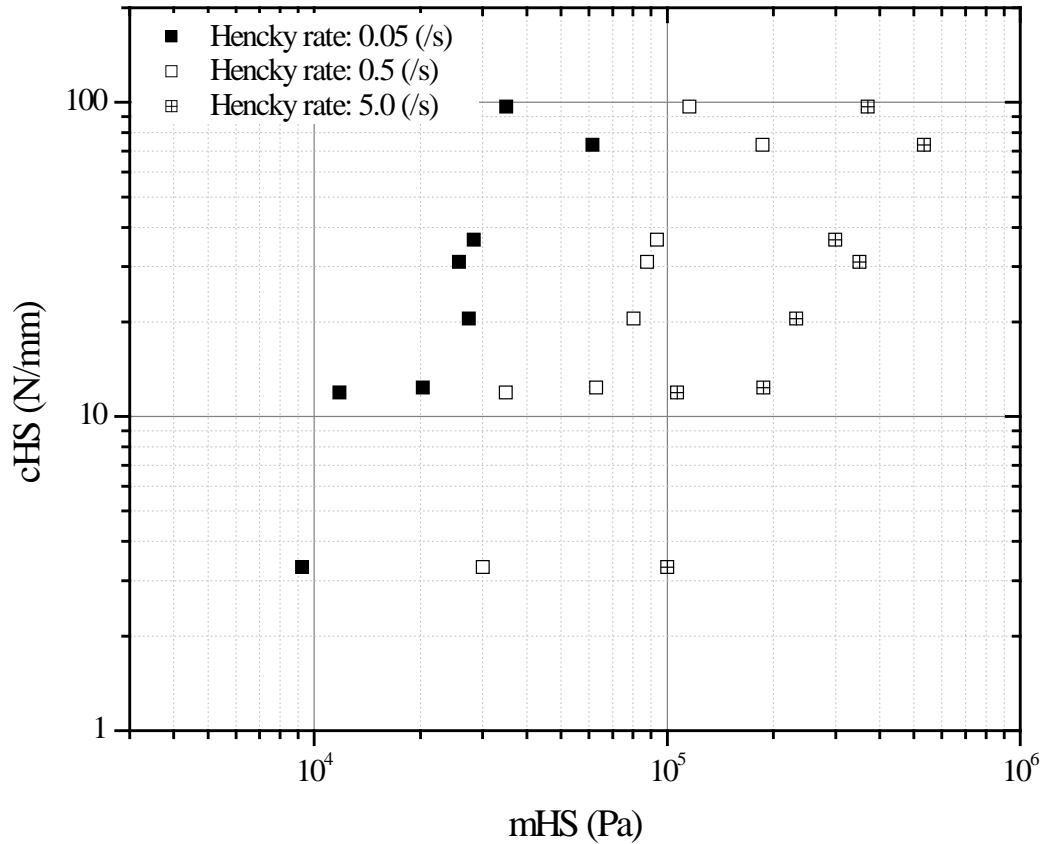
Figure 2. cHS vs. mHS trends (see Sardashti et al.[2] for details on Hencky rate).

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.[3,6]

Finally, a well-controlled ultraviolet (UV) photo-initiated 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 four-fold increase in ESCR, was achieved with minimum polymer degradation or crosslinking.[3,16]

Ultimately, the four stages of the research, as briefly described above, can lead to a set of suggestions/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 rather unreliable (noisy) indicator (ESCR), with a more fundamental property (hardening stiffness, from a stress-strain test), which is more precise and reliable. As such, it might be 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 current publication describes the culmination of the four stages of research, as outlined above. As a quick overview, one can start with mechanical (and rheological) testing that leads to the suggestion of new indicators for evaluating ESCR of different PE resins. One can then

continue with the construction of different property 'maps', relating important PE properties such as density, molecular weight, crystallinity, and ESCR. These extremely useful operational maps would allow one to select the appropriate PE resins for a specific performance target. The construction and use of these maps is the topic of the current publication.

2. Experimental and Characterization

2.1 Materials

A wide range of commercially available PE resins (18 in total) were selected (see **Table 1**). These resins included four rotational molding grade LLDPE type resins, and fourteen HDPEs. Selected HDPE resins consisted of three rotational molding grades, one injection molding grade, four blow molding, and six pipe resins (two PE 80, and four PE 100 type pipe resins).

These resins were selected in order to cover a wide range of molecular structures and ESCR values, to develop a clearer understanding of potential relationships between important molecular structural characteristics and ESCR. For practical purposes, polyethylene homopolymers with narrower MWD were not considered in this study as such PEs typically have very low ESCR values [17]. In Table 1, the symbols represent average molecular weights (weight average, Mw, number average, Mn, and z-average, Mz), polydispersity index (PDI), and short chain branching (SCB) (these measured variables will be revisited below). Additional explanations are given directly below the table.

Table 1. Molecular Properties of PE Resins

PE ID	PE grade	Density (kg/m^3)	Mn (kg/mol)	Mw (kg/mol)	Mz (kg/mol)	PDI (Mw/Mn)	SCB[a] (/1000C)	ESCR[b] (h)
LLDPE 1	R.T.[1]	936	15.4	71.8	252.0	4.7	4.2	60
LLDPE 2	R.T.	938	20.8	82.0	232.0	3.9	7.5	150
LLDPE 3	R.T.	937	18.0	74.6	191.0	4.0	13.3	190
LLDPE 4	R.T.	932	15.1	76.6	286.0	5.1	22.3	650
HDPE 1	R.T.	948	18.7	77.9	349.0	4.2	1.6	8
HDPE 2	R.T.	942	25.2	118.5	336.0	4.7	2.4	50
HDPE 3	Pipe-100[2]	958	10.4	217.9	1244.2	20.9	7.0	1000
HDPE 4	Pipe-100	955	5.9	315.4	2129.3	53.3	11.8	3000
PE 4	I.M.[3]	948	19.7	79.4	239.3	4.0	3.8	18
PE 8	Pipe-80[4]	958	14.0	202.1	1398.4	14.4	4.5	>500
P1	B.M.[5]	948	14.8	258.3	2176.6	17.5	3.0	500
P2	B.M.	957	12.5	193.3	1779.2	15.4	1.2	40
P3	B.M.	954	10.8	209.2	1617.0	19.4	4.0	300
P4	B.M.	965	10.4	182.0	159.1	17.5	2.6	15
P5*	Pipe-100	959	---	260.3	---	---	5.6	>1000
P6*	Pipe-100	948	---	301.5	---	---	11.9	>5000
P7*	Pipe-80	951	---	168.7	---	---	11.3	2000
P11	R.T.	---	18.0	126.5	905.3	7.0	2.2	21

* PE with pigments (No GPC was performed, MW averages were not measured, the reported Mw was found from rheological methodologies[18]); [a] Short chain branching per 1000 carbon atoms; [b] ESCR reported from a Bent Strip Test (BST) according to ASTM D1693A; [1] Rotational molding grade PE; [2] PE100 grade pipe resin; [3] Injection molding grade PE; [4] PE80 grade pipe resin; [5] Blow molding grade PE

2.2 Characterization Techniques

Multiple techniques were used to characterize the PE resins. Details of each technique are briefly described in the following subsections. Results for each resin are summarized in **Tables 1 and 2**.

Table 2. Additional Molecular Properties of PE Resins

Polymer ID	X (%)[a]	l (nm)[b]	LSA (nm^2/mol)[c]	HS (N/mm)[d]	cHS (N/mm)[e]
LLDPE 1	49.41	10.86	3.3	0.249	2.68
LLDPE 2	48.90	11.15	3.7	0.336	7.38
LLDPE 3	46.90	10.76	3.3	0.269	9.53
LLDPE 4	42.38	10.77	3.1	0.3	18.3
HDPE 1	59.69	13.71	3.4	0.214	0.95
HDPE 2	55.19	12.87	5.2	0.352	3.55
HDPE 3	61.5	14.6	9.3	0.536	29.2
HDPE 4	51.5	11.7	14.1	0.55	73.11
PE 4	58.4	13.16	3.6	0.22	2.37
PE 8	58.1	13.52	8.8	0.38	12.34
P1	64.4	15.44	10.9	0.74	20.48
P2	72.7	18.09	7.8	0.40	3.31
P3	70.8	15.97	9.3	0.40	11.92
P4	80.6	20.48	7.2	---	---
P5	63.0	14.15	11.4	0.70	36.46
P6	62.3	14.34	13.3	0.75	96.74
P7	55.9	12.98	11.4	0.46	30.99
P11	66.3	15.07	5.6	---	---

[a] percentage crystallinity; [b] lamella thickness; [c] Lamella Surface Area; [d] Hardening Stiffness; [e] Corrected Hardening Stiffness

2.2.1 Differential Scanning Calorimetry (DSC)

Resin crystallinity and lamella dimensions were assessed by DSC analyses, performed with a Q2000 DSC controlled by a TA processor. In order to clear their thermal history, samples were heated at a rate of 10 ºC/min from room temperature (21 ºC) to 240 ºC, followed by a 3 min isothermal step under a nitrogen environment. Ultimately, samples were subjected to a cooling cycle and a second heating cycle, both at a rate of 10 ºC/min, to obtain the DSC peaks.

2.2.2 Gel Permeation Chromatography (GPC)

Molecular properties, namely, average molecular weights (weight average, Mw, number average, Mn, and z-average, Mz), molecular weight distribution (MWD), and polydispersity index (PDI) were evaluated by GPC. The GPC analysis was performed on a high speed GPC from Polymer CHAR (Spain), with a viscometer (Viscotek 150R), and a light scattering detector. The GPC was also equipped with an infra-red detector (GPC-IR5) for determination of short branching content and branching distribution. The analysis was done using high temperature (140 °C) and 1,2,4-trichlorobenzene (TCB) as the solvent. Each GPC sample contained 1.67 mg PE in 1 ml of TCB. GPC calibration was based on a conventional approach with narrow polystyrene standards.

2.2.3 Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR)

^{13}C NMR spectroscopy has been extensively used to quantify branching content in polymers. The largest peak in an NMR spectrum represents the backbone C-C bonds in PE. The number of branches per thousand carbon atoms can be calculated by dividing the area under the branching peak by the area under the backbone peak. It should be noted that a disadvantage of ^{13}C NMR is that it is unable to measure branched chains longer than six carbons. In this work, ^{13}C NMR was mainly used to identify the extent of short chain branches in the polymer. An AVANCE 500 Bruker NMR was utilized to investigate the short chain branching (SCB) content of the PE resins at 120 ºC. The solvent of choice was deuterated TCB.

2.2.4 X-ray Diffraction (XRD)

Two types of X-ray diffraction (XRD) techniques were used in this work. For both techniques, bars 25 mm in length and 10 mm in width were compression-molded at 190 °C and 44.5 kN, followed by quenching in cold water.

The first technique was wide-angle X-ray scattering (WAXS), in which the scattering angles were from 6° - 34°. WAXS patterns were measured in a STOE two circle goniometer using Cu Kalfa radiation from an ENRAF NONIUS FR 571 rotating anode generator. To minimize the background level, the X-rays were detected with a MOXTEK energy sensitive Si-detector, connected to single channel analyzers that selected photons corresponding to the Cu Kalfa radiation (Lambda (λ) = 1.54178 Å). WAXS was conducted to identify the X-ray percentage crystallinity (X %) of the PE resins (ratio of the area under the crystalline peak to the total area of the X-ray scan).

The second technique was small-angle X-ray scattering (SAXS), which was used to find the long spacing (L) and, consequently, the lamella thickness (l) of the resins. The SAXS patterns were measured in a Bruker NANOSTAR using Kalfa radiation.

2.2.5 Hardening Stiffness (HS)

The tensile tests were performed at room temperature (21 °C) on an Instron 3365 machine. The specimens were prepared by punching compression molded plaques prepared at two different processing conditions:

Condition 1: Compression molding at 195 ℃ ± 5 ℃ and 44.5 kN. The plates were allowed to cool down in the mold at room temperature over a period of 24 hours.

Condition 2: Compression molding at 195 ℃ ± 5 ℃ and 44.5 kN, followed by cooling to room temperature at a rate of 1 ℃/min, while increasing the pressure to 89 kN.

The HS was obtained by measuring the slope of the strain hardening section of the load-displacement curve. The test specimens were extended until complete failure was obtained at a rate of 10 mm/min.

2.2.6 Notch Constant Load Test (NCLT)

The NCLT according to ASTM D5397 was utilized to identify the ESCR of the resins. In this test, specimens were subjected to constant load under an aggressive environment at elevated temperatures. A notch was introduced in the compression-molded, dog-bone samples that had been prepared at 190 ℃, producing a ligament thickness of 60 % of the nominal thickness of the specimens. The notched specimens were suspended in a solution of water and 10 % surfactant (Igepal) under an applied stress equivalent to 15 % of the yield stress. The time of failure was recorded and reported as the ESCR of the resins. It should be mentioned that NCLT was used to selectively verify the ESCR reported from a Bent Strip Test (BST, which is one of the preferred conventional methodologies to evaluate ESCR), provided by the resin manufacturer.

2.2.7 Oscillatory Shear Rheometry

A TA Instruments AR2000 rheometer with parallel plate geometry was used to measure the shear properties. Both oscillatory shear experiments and shear creep tests were performed to measure the linear viscoelastic properties of the polymers. All PE resins were compression molded into 25 mm disks at 190 ºC and 44.5 kN, followed by quenching in cold water. Prior to frequency sweeps, strain sweeps between 0.1 - 100 % strains were performed at 100 Hz at 150 ºC and 190 ºC, to identify the linear viscoelastic region of the PE samples. Further, time sweeps at the specified temperatures were conducted in order to identify any degradation or crosslinking during the frequency sweeps. Then, a series of frequency sweeps were carried out at frequencies (ω) between 0.01 - 100 Hz under nitrogen. Shear creep tests were also conducted at 150 ºC and 190 ºC on compression molded disks. Creep experiments were conducted at 10 Pa (linear viscoelastic region) for 3 hours. It should be noted that all the rheological experiments were independently replicated at least three times to ensure good reproducibility in the results.

2.2.8 Capillary Rheometry

One of the most common methods to characterize polymer behaviour at high shear rates is capillary rheometry, since one is able to identify the polymer behaviour subjected to real processing conditions under extrusion or injection molding. A bench top, twin bore Rosand capillary rheometer (RH2200 series) manufactured by Malvern was used to measure the shear

viscosity and entrance pressure drop. Due to the twin bore option, simultaneous measurements were made using a long die and a zero length die. The long die was used to determine shear properties, while the zero length die provided the entrance pressure drops due to the sudden barrel contraction (between the capillary reservoir and capillary die). In order to identify the entrance pressure drop at various shear rates, three different pressure transducers were used. A 250 psi and a 1500 psi transducer were separately attached to the bore (reference bore) equipped with the zero length die (orifice) to measure the entrance pressure drops. A 5000 psi transducer was attached to the sample bore, equipped with the long die to measure the shear viscosities at various shear rates. Ultimately, the entrance pressure drops obtained from the reference bore were used to correct the applied stress data (reflected on the viscosity measurements).

2.2.9 Sentmanat Extensional Rheometry (SER)

The transient uniaxial extensional viscosity, η_E, was determined at 150 $^{\circ}$C and 190 $^{\circ}$C on a Sentmanat Extensional Rheometer SER-HV-A01 model attached to an ARES 2000 rotational rheometer. The extensional rheology specimens were prepared by compression molding PE pellets to create thin sheets. The sample width was fixed at 12.7 mm (prepared by a calibrated dual blade cutter) and the thickness was 0.65 mm (measured precisely before each test by a micrometer). Maximum Hencky strains of up to 5.6 can be achieved with this instrument. Note that the steady state extensional viscosity data were taken from the peaks appearing on the transient viscosity curves for the corresponding extensional strain rates.

3. Molecular Properties Affecting ESCR

The main molecular properties affecting the ESCR of PE are molecular weight and short chain branching content and their distributions. Crystallinity also plays an important part in controlling ESCR. A brief description of the effect of each of these molecular properties on ESCR is given in the following subsections.

3.1 Molecular Weight (MW) and Molecular Weight Distribution (MWD)

The failure mechanism involved in ESCR is a disentanglement process that can take place in two main regions: (1) the interface between the amorphous and crystalline regions, and (2) the amorphous region. The disentanglement in the interface mainly involves tie-molecules that connect the crystalline lamellae to the amorphous region. Therefore, the higher the content of tie-molecules in PE, the higher is the ESCR. The rate of formation of tie-molecules is directly controlled by the MW of the polymer. PEs with higher MW, have a higher density of tie-molecules,[19] hence, a higher resistance to rate of molecular disentanglement is expected. Similarly, van der Waals forces between the physical chain entanglements in the amorphous region (including inter-lamellar links, cilias, and loose loops) have been shown to enhance ESCR.[9] Higher MW can increase the degree of such inter-lamellar connections, thus promoting ESCR. MW values in the vicinity of 150 kg/mol are required to create a sufficiently high density of tie-molecules for an enhancement in ESCR.[20]

PE resins are composed of chains with different lengths, resulting in a molecular weight distribution. MWDs can be unimodal or bimodal/multimodal. In general, PE homopolymers with a narrow unimodal MWD have low ESCR [17]. Incorporation of a large amount of short chain branches can enhance the ESCR in this type of PE; however, addition of a large amount of short branches can cause a deterioration of other mechanical properties, such as stiffness, needed for PEs in structural applications. PEs with bimodal MWD, show a relatively higher ESCR. The low(er) molecular weight fraction of the MWD can enhance the crystalline state of the polymer and increase its fracture toughness,[21] whereas the high(er) molecular weight fraction can assist in the formation of a large number of tie-molecules, which ultimately increases ESCR. For an overall superior mechanical performance, a proper balance between the ratio of low and high molecular weight fractions is required. In general, for applications where a high ESCR is needed, a large fraction of the high molecular weight portion is preferred. PE100 pipe resins, with extremely high ESCR, have a small fraction ratio between the low and high MW fractions.

3.2 Short Chain Branching (SCB) Content and Distribution

Incorporation of short chain branches in PE increases ESCR. The enhancement in ESCR is directly related to the formation of a higher number of effective tie-molecules as a result of the addition of short branches (both length and frequency of SCB). Furthermore, the distribution of SCB over the MWD is very important. For unimodal MWD PEs, most of short chain branches are formed in the lower end of the MWD spectrum. These short chain branches, although effective in increasing resistance to crack growth, are not contributing to a large

enhancement of ESCR. On the other hand, in bimodal MWD PEs, addition of SCB in the high molecular weight fraction of the distribution can significantly increase ESCR.

3.3 Crystallinity and Density

Crystallinity and density of PE can be controlled by the amount of short chain branches. An increase in the amount of SCB generally reduces the percentage crystallinity and consequently the density of PE; however, it is still difficult to develop a reliable equation to relate the SCB content to either percentage crystallinity or density.[11] Failure to develop such a correlation has been attributed to differences in other factors such as MW, and type and distribution of short branches. Similarly, it is not feasible to develop a simple relationship between ESCR and crystallinity/density. Assuming that MW and type/distribution of branching are constant, any decrease in crystallinity/density (as a result of an increase in short branches), would increase ESCR. On the other hand, an increase in crystallinity for PEs with relatively high MW was observed to increase ESCR.[3] This was related to an increase in the stiffness and fracture toughness of the material, which ultimately reduced the rate of crack growth propagation. Crystallinity/density and hence their effects on ESCR can be controlled by processing temperature. Post-processing isothermal annealing at different temperatures and periods reduces the number of tie-molecules (enhancement in crystallinity/density) and reduces ESCR.[3] On the other hand, fast cooling can improve ESCR.

4. Structure-Property Relationships with respect to ESCR

4.1 Construction of Maps

Structure-property relationships with respect to ESCR can be summarized using operational property maps, which correlate measurable properties with ESCR. These 'maps' offer 'windows' into the whole process and its complex nature/events. **Figure 3** represents relationships between MW, SCB (at different MW levels), MWD (at different MW), and ESCR. Since ESCR is highly influenced by MW, the resins were separated into two groups according to their weight average molecular weight (Mw), high MW (PE resins with Mw above 170 kg/mol) and low MW (PE resins with Mw around or below 120 kg/mol).

While ESCR of HDPE scales with MW,[2-4] an increase in MW does not necessarily increase ESCR for an HDPE homopolymer (see Figure 3 (a), where the lowest point of the high MW group (P 4) shows a lower ESCR compared to the low MW group members). Increasing MW in HDPE homopolymers mostly adds to the crystallinity of the polymer, hence, no considerable enhancement in ESCR is expected. Figure 3 (b) illustrates the effect of SCB on ESCR for PEs with different MWs. As shown in Figure 3, ESCR increases with SCB content; however, the extent of such an increase is different for PEs with different MW levels. The low MW group, even at the highest SCB level (23 / 1000 carbon atoms), can only achieve an ESCR of around 650 h. On the other hand, the high MW group can simply reach high values of ESCR (above 1000 h), with SCB of less than 6 / 1000 carbon atoms. This observation validated the synergistic effect of MW and SCB on enhancing ESCR. The relationship between ESCR and polydispersity index (PDI: Mw/Mn) obtained from MWD is shown in Figure 3 (c). It was not

possible to develop a clear relationship between ESCR and PDI (as is usually the case with distributional properties). In both MW groups, PDI (representing the breadth of the molecular weight distribution) did not have a significant effect on ESCR. This was associated with differences in MW and SCB content (and distribution), which have a stronger influence on ESCR.

Figure 4 summarizes the steps involved in rationalizing a relationship between density and ESCR. Figure 4 (a) represents the increasing linear relationship between crystallinity and density for the low MW group. This relationship is more complex for the high MW group (although still increasing), due to the potentially large differences in SCB content, SCB distribution, and the differences between the ratio of low and high MW fractions of the MWD (most members of the high MW group are PEs with bimodal MW distributions). Figure 4 (b) highlights the relationship between crystallinity and MW. It was found that crystallinity scales with MW for the low MW group. It should be noted that the crystallinity of the LLDPEs (which are part of the low MW group) was completely controlled by SCB content, not MW. The relationship between crystallinity and MW, however, is reversed for the high MW group, where an increase in MW reduces crystallinity. Based on this observation, it can be concluded that the effect of SCB on the density/crystallinity of the high MW group is negligible. Therefore, the density of such high MW PEs is mainly controlled by their MW. Figure 4 (c) ultimately displays the relationship between ESCR and density. Both MW groups showed a decreasing trend in ESCR with density; however, the density of the high MW group was significantly higher, representing a larger resistance to crack propagation and higher fracture

toughness. The large density of the high MW group qualifies such resins for pipe applications, where large fracture toughness values are required.

Based on these observations, several diagrams, shown in **Figure 5**, were developed for a better representation of the relationships between different molecular structure characteristics and ESCR. These diagrams were developed based on the PEs in this study, offering pathways to develop polymers with a wide range of properties and applications. This 'map' is a 'diagram compendium' that shows the direct relationships between major molecular structure characteristics, and their possible interactions with ESCR. Another important fact is that the effect of SCB content is reflected on crystallinity and density. Therefore, this map eliminates the need for explicit inclusion of SCB content measures.
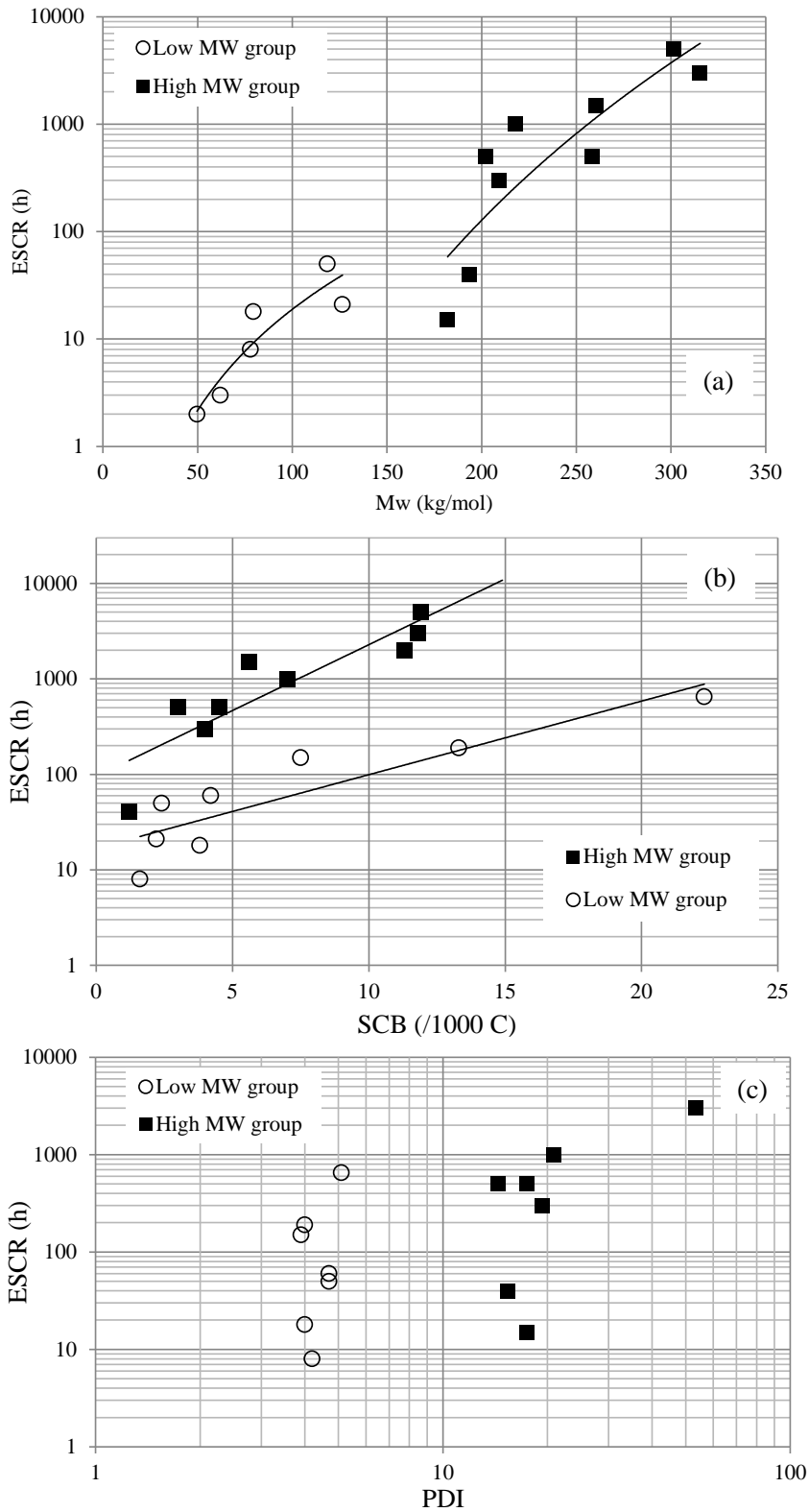
Figure 3. Effect of weight average MW, SCB, and PDI of MWD on ESCR
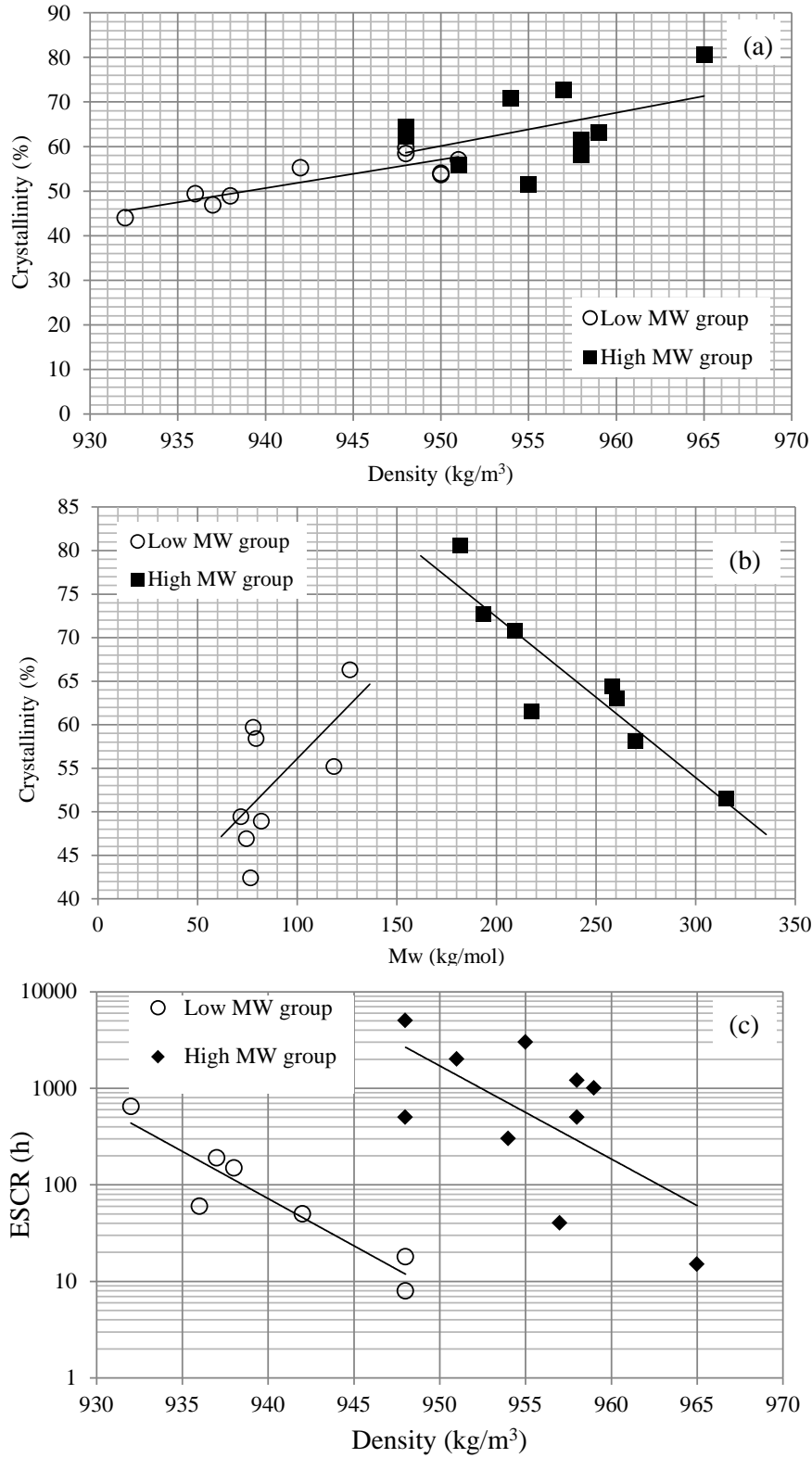
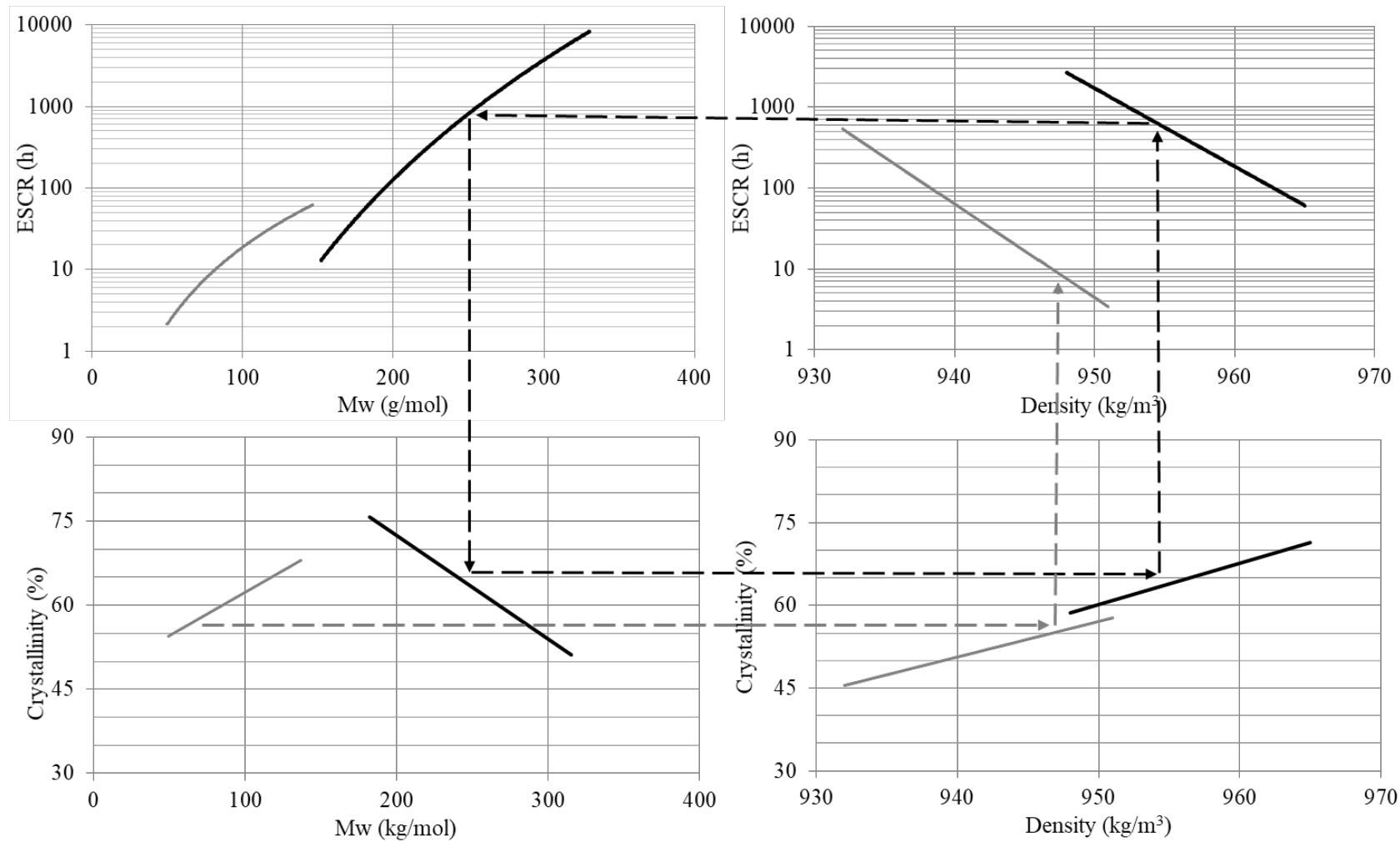*Figure 4.* Relationship between MW, percentage crystallinity, density and ESCR

Figure 5. ESCR and molecular structure mapping

4.2 Interpreting the Maps

The plots in the mapping of Figure 5 are set up such that given the weight average molecular weight of a PE resin, the crystallinity, density, and most importantly, ESCR can be estimated based on the correlations between those properties. By connecting the curves/lines on each plot in the map (see dashed black line in Figure 5), the remaining properties can be estimated. For example, following the dotted black line (square) on Figure 5, a PE resin with a high MW of 240 kg/mol, would have an estimated crystallinity, density, and ESCR of 66 %, 954 kg/m^3, and 800 h, respectively. Similarly, following the dotted grey line in Figure 5, the crystallinity, density, and ESCR can be estimated for a low MW PE resin. In addition, these maps can be used to determine the crystallinity, density, and MW (either high or low MW) needed for a PE resin based on the required ESCR for a given application.

It should be noted that the maps shown in Figure 5 were developed based on a rather wide range of PE resins/grades. However, one can never cover all possible resins or grades; this is the nature of almost any effort to derive structure-property relationships. Therefore, this map should be used more reliably for the evaluation/estimation/prediction of ESCR, when the molecular properties of the selected PEs fall in the same operating vicinity/range as the ones used in this work.

5. Prescriptions and Case Studies

5.1 Prescriptive Pathways

In addition to the mapping of typical resin structural characteristics (Figure 5), a "prescriptive pathway" for selecting a PE with higher (or optimal) ESCR is presented in **Figure 6**. This figure is a modification of a similar diagram, originally suggested by Cheng et al.,[5,6,17] that contains a series of questions for the selection of a PE grade with desirable ESCR . Steps shown in Figure 6 are given based on a collection of observed relationships between various molecular properties and ESCR. This diagram summarizes the efforts conducted in both the solid and melt states, through various characterization techniques, to provide a proper measure/indicator of the ESCR of PE resins.
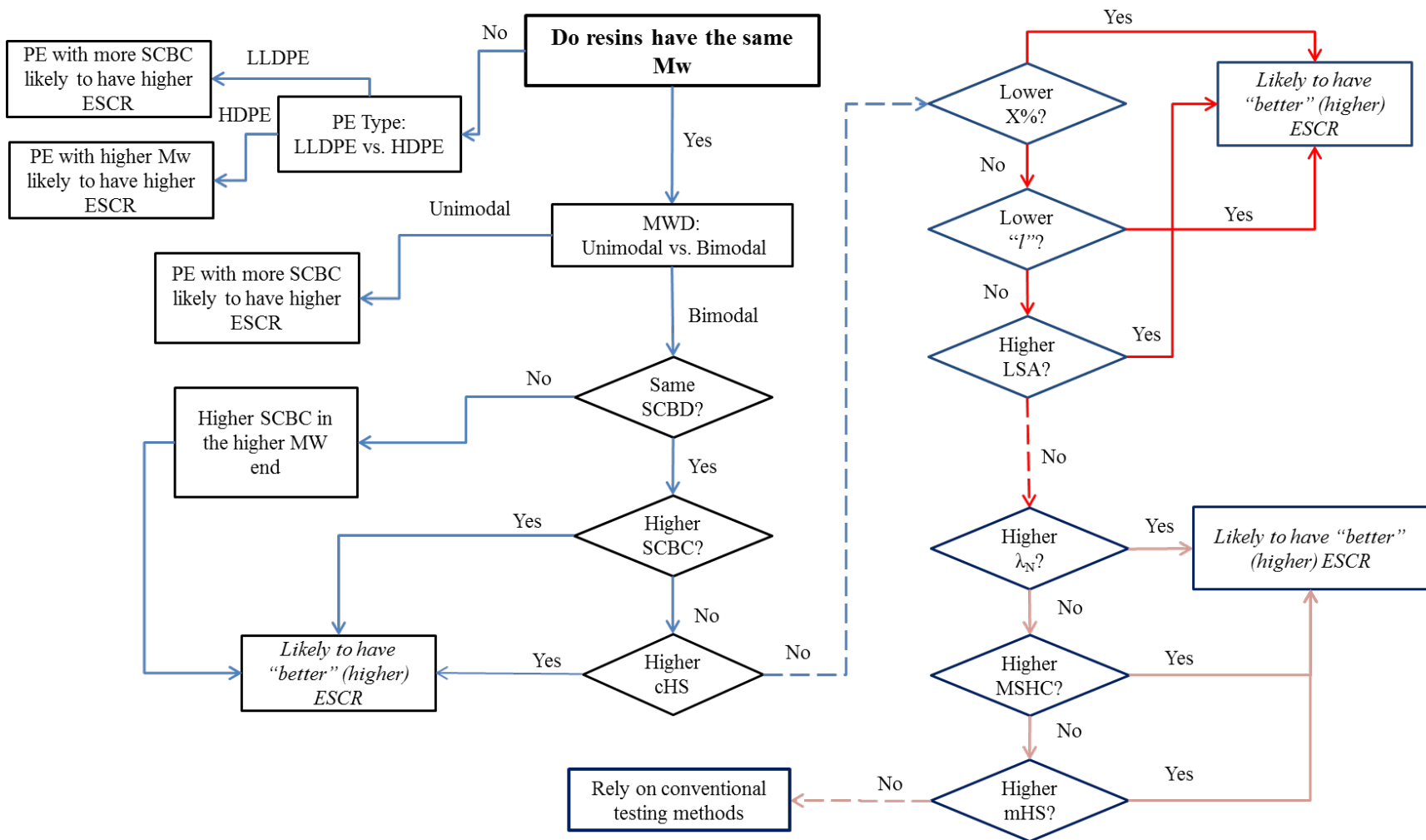
Figure 6. Prescriptive pathways for selecting a PE with better/higher ESCR. Note: Mw is molecular weight, MWD is molecular weight distribution, SCBC is short chain branching content, cHS is corrected hardening stiffness, X% is percent crystalinity, l is lamella thickness, LSA is lamella surface area, λ_N is molecular weight-normalized average characteristic relaxation time, MSHC is melt strain hardenning coefficient, mHS is melt hardening stiffness. (See also Tables 1 and 2).

5.2 Prescriptive Case Studies

In order to verify the reliability of the developed operational maps, diagnostic checks were conducted to identify and demonstrate the predictive capabilities of the suggested correlations, using three "unknown resins" (hence, the final check was like a 'blind' test). Molecular properties of the unknown resins were investigated and ultimately employed along with the developed diagrams to identify the "ESCR range" of the unknown resins. Three PE resins, which included two injection molding PE grades (see subsection 5.2.1 and 5.2.2) and a blow molding PE grade (see subsection 5.2.3), were characterized, according to the techniques described in Section 2.2. They were subsequently used as prescriptive examples in order to obtain estimates of some of their properties based on a minimum of characteristics, for evaluating the effectiveness of the ESCR-(micro)structure maps. Given their weight average molecular weight (Mw), the percentage crystallinity, density, and ESCR were estimated using the ESCR-structure map in **Figure 7**. (Of course, one could also use the maps of Figures 5 and 7 and move 'backwards', i.e., traverse the inverse path and identify properties of a PE grade based on a desirable ESCR range.) Each of these resin properties was measured using appropriate characterization techniques. The following case studies demonstrate the validity of these structure-property correlations and the effectiveness of these maps.

5.2.1 Case Study 1: Mw = 50 kg/mol

The first unknown resin (PE 1) is an injection molding PE grade, with relatively high melt flow index. Characterization techniques (described in Section 2.2) were carried out to identify the

weight average molecular weight of PE 1 (Mw=50 kg/mol). Figure 7 offers a crystallinity-Mw

correlation (left bottom figure, low MW group) for such a low Mw PE. This correlation indicated

a percentage crystallinity of 54.6 % for PE 1. For a 54.6 % crystallinity, the correlation developed

between percentage crystallinity and density is available in Figure 7 (right bottom figure, low MW

group). This correlation indicated a density of around 947 kg/m^3. Ultimately, using the correlation

between ESCR and density (top right figure, low MW group), suggested an ESCR value of around

7 h for PE 1. The resin manufacturer reported an ESCR of 3 h for PE 1, based on a bent strip test

(BST). The percentage crystallinity of PE 1, according to DSC, was also evaluated and was found

to be 54 %.   Both ESCR and percentage crystallinity obtained from the correlation and

characterization techniques were similar, verifying the reliability of the developed correlations.

5.2.2 Case Study 2: Mw = 62 kg/mol

The second 'blind-test' resin (PE 2), also an injection molding PE grade, was characterized and a

weight average molecular weight (Mw) of 62.0 kg/mol was obtained. A similar methodology was

conducted to find the resin properties from the diagrams of Figure 7. Mw of 62 kg/mol

corresponded to a percentage crystallinity of about 56.5 % (using the low MW group correlation),

a density of 950 kg/m^3, and an ESCR value of around 4 h. The BST and characterization by DSC

indicated an ESCR value of 2 h and a percentage crystallinity of 57 %, once again verifying the

reliability of the correlations for PEs with relatively low molecular weight and low densities.

5.2.3 Case Study 3: Mw = 127 kg/mol

The third resin (PE 3), a blow molding PE grade, had a relatively higher Mw of 127 kg/mol, corresponding to a percentage crystallinity of 66.47 % obtained from the low MW group correlation. For this resin, the crystallinity-density correlation, and ESCR-density from the high MW group is available, providing a density value of 958.4 kg/mol, and an ESCR value of close to 827 h. The company reported an ESCR of about 1000 h for this resin, which is very similar to what we found from the developed correlations in this work. However, the determined percentage crystallinity (54 %) was significantly lower than the value obtained from the correlations. The difference between the determined and predicted percentage crystallinity is attributed to the lack of fit of the crystallinity-Mw curve for the low MW group. In order to enhance the predictability of this correlation, PEs with molecular weights between 120-150 kg/mol, and different short chain branching contents, should be added to fill the gap.
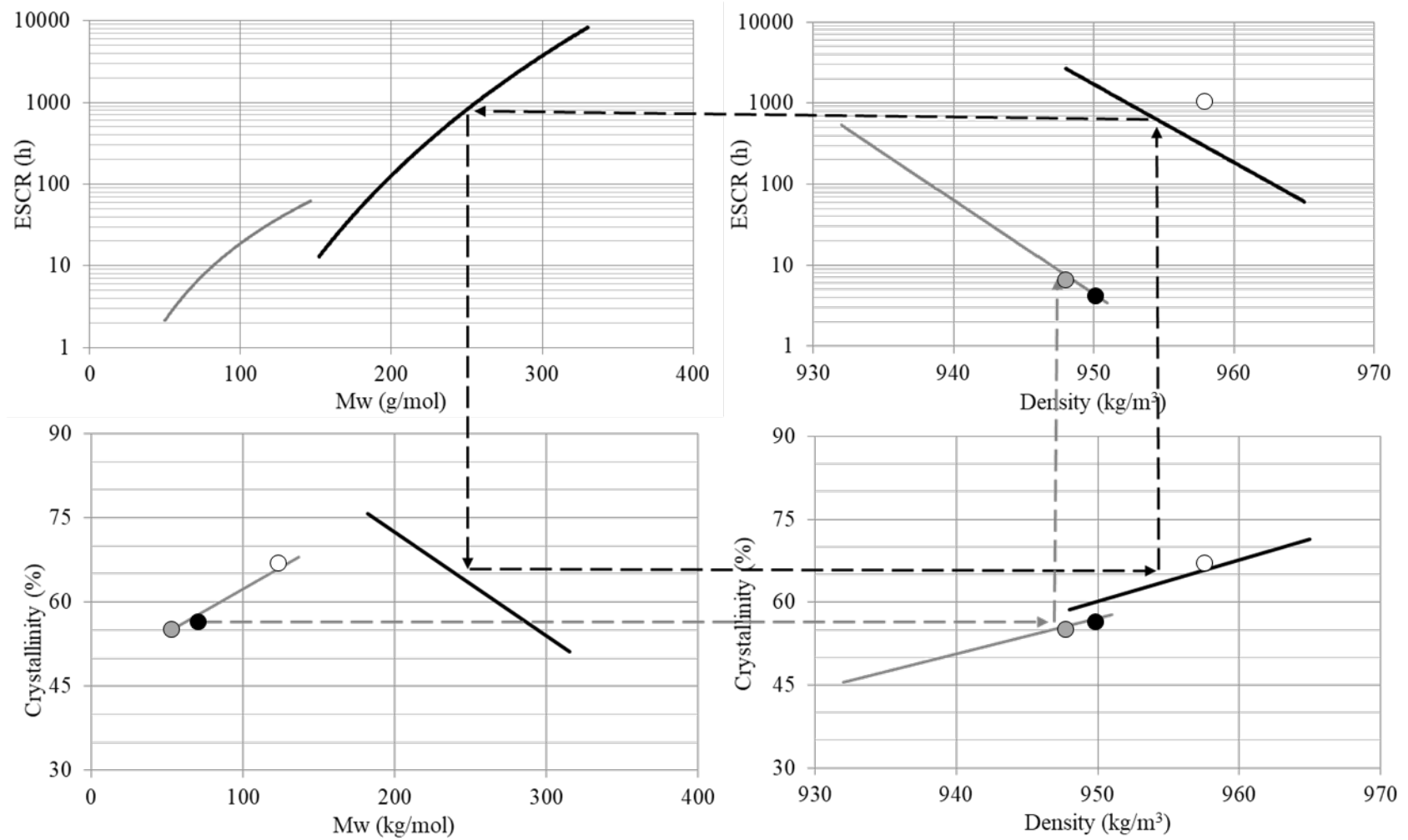
Figure 7. ESCR and molecular structure map showing the data for Case Study 1 (grey circles), Case Study 2 (black circles), and Case Study 3 (white circles).

6. Concluding Remarks

A general overview of the relationship between major molecular structure characteristics and ESCR of PE resins, based on experimental characterization and published literature trends, has been provided. Furthermore, relationships were developed between ESCR, Mw, percentage crystallinity, and density to indicate the influence of each factor, and potentially their interaction, on the ESCR level. Ultimately, several diagrams were developed based on all the experimental observations, displaying the developed correlation 'maps' (see Figures 5 and 7). In addition, a logical flowchart was suggested that offers practical prescriptions and describes pathways towards the development of PE with a desirable (better/higher) ESCR (see Figure 6).

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Demonstration of structure-property maps which correlate various molecular properties and environmental stress cracking resistance (ESCR) of polyethylene (PE). These maps, along with prescriptive pathways, can be used to improve the development of PE resins with a desirable (better/higher) ESCR.

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Operational Maps Between Molecular Properties and Environmental Stress Cracking Resistance (ESCR)