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Design of Polymeric Materials: Experiences and Prescriptions

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Abstract

As process engineering has matured, research interest has shifted towards polymer product quality. In the past 20 years or so, the shift has progressed even further, as interest in polymer product quality has morphed into polymer product design. Product design is intended to be a targeted pursuit of optimal conditions that will yield polymers with desirable properties for a specific application. This can be achieved by following a systematic design framework that employs sequential, iterative steps informed by prior knowledge and experience. This overview provides some background information regarding the need for design (including some examples from previous experience), especially in terms of structure-property relationships. When links between kinetics (synthesis conditions), polymer structure, and application properties are well-understood, it becomes possible to essentially ‘reverse-engineer’ the polymeric material; the researcher can start with known application requirements and synthesize polymers with tailor-made properties using an optimized recipe (according to the polymerization kinetics). A suggested design approach is presented herein, followed by the application of the design approach to two large case studies. The number of applications for polymeric materials is essentially limitless; the current work provides typical examples of a systematic polymeric material design framework (and related case studies).

Keywords: polymeric material design; polymers; polyolefins; sensing materials; water-soluble polymers

1. INTRODUCTION

The wide variety (and subsequent versatility) of available polymeric materials is extremely attractive from a design standpoint. Polymers are typically inexpensive (in terms of both materials cost and processing cost), lightweight, and have tailorable application properties. As a result, they are employed as foams, fibres, films, and bulk molded materials.

The range of polymeric materials available for engineering applications can be overwhelming. Technical data are typically available once a material is selected, but how is that initial selection made? How can that material be tailored for a specific application? Many scientists and engineers use trial-and-error approaches; often the synthesis is the priority, and finding a suitable application is an afterthought. In other cases, researchers may have an application in mind, and they try various recipes until they are satisfied with the result. However, both of these approaches are ineffective. Not only are valuable experimental resources wasted during the trial-and-error stage, but there is also no guarantee that the polymer products have been optimized for the specific application.

As material requirements for particular applications become more specific and strict, using a targeted approach to design polymeric materials becomes a necessity. Following a general design framework prevents researchers from using trial-and-error approaches or ‘shoehorning’ materials into applications for which they are non-optimal. To obtain polymer products with desirable properties (both fundamental characteristics and for a specific application), one must always begin with an awareness of existing materials and methods. This background knowledge informs preliminary design of experiments, which in turn provides insight for additional experiments to synthesize (and characterize) optimally designed materials.

The overarching motivation to use a design approach is to make full use of available resources and to efficiently work towards the identification, synthesis, characterization, and eventual application of polymer products with optimal properties. Therefore, the design of polymeric materials (through exploring structure-property relationships and making use of established design frameworks) is essential.

2. BACKGROUND

We will start with a brief and rather broad historical perspective, in order to put the main theme of this article in context. What we usually refer to nowadays as ‘macromolecular science’ started in the late 1800s and saw many advances in the first 30-40 years of the 1900s as polymer science and polymer technology, based mainly on fundamentals of physical, analytical and organic chemistry. With the establishment of the existence of these ‘big or giant molecules’, rapid advances took place in both academic and industrial circles, with the main emphasis on the synthesis of new polymer molecules, that led to commodity products (nylons, polyesters, rubbers). In the 1940s-1960s, advances in polymer chemistry/technology and the synthesis of these macromolecules naturally led to larger production scales, with polymer engineering coming into play (batch and continuous reactors). The gamut of polymer products became now wider, including paints, coatings, adhesives, rubbers, plastisols, etc. Polymer characterization, advances in catalytic polymerization processes, and polymer processing/rheology opened new vistas, and expanded polymer science/engineering (now including high quality polyolefins). We now moved from polymer synthesis on the chemistry bench to polymer reaction engineering, reactor scale-up and mathematical modelling of these polymer production systems (polymer production technology), with emphasis on increasing productivity. The new market mix (in the 1960s-1980s) included a wide range of commodity and specialty products. Free radical and ionic/coordinated polymerizations as well as bulk/solution/emulsion/dispersion types of processes became more established. All sorts of innovative reactor technologies (batch, semi-continuous, continuous trains) and all sorts of operating conditions (low to elevated temperatures and pressures) and reactor operation regimes (isothermal, temperature programming, intermittent feed streams, etc.) were investigated and employed. All sorts of polymeric chains (homo-, co-, ter-polymers and other multicomponent polymers) and several architectures (linear, branched, crosslinked) could be synthesized. Polymer processing/modification (reactive or not) and polymer characterization became almost separate branches (in their own right) of the polymer science/engineering continuum.

Macromolecular science/engineering (including all other complementary branches) developed considerably during the period starting around the 1960s and culminating into the 1980s-1990s.

As it evolved further, it saw the major emphasis on process engineering, using such tools as mathematical modelling, optimization and control techniques, in order to maximize productivity. In parallel, product quality (a much more difficult consideration) started becoming of import for evident reasons (better control over the polymer chain properties and hence application performance, cost/profit, etc.). Still, the main idea and emphasis were on how to move optimally from a certain reactor input (formulation) and operating conditions to the reactor output, and deliver the product/resin to the next stage (processor, user). Polymer characterization (for composition, molecular weight, sequence length, branching indicators, both on average and distributional properties) contributed tremendously towards a better understanding of the produced chain microstructure.

In essence, this trajectory from multicomponent polymerization kinetics (polymer synthesis) to polymer reactor design, modelling, optimization and control gave us increased production rates and improved understanding on polymeric molecule (chain) microstructure indicators (polymer quality). One could use polymer reaction engineering and polymer characterization tools to go from the process/reactor input to the process/reactor output. What happened in parallel in the mid-90s was the so-called ‘quality’ revolution, with synchronous advances in statistical process/quality control (triggered by industrial sectors, e.g., automobile and automobile parts manufacturing) and substantial improvements in solid-state micro-electronics (physics) and computer technology (in both hardware and software). Now equipped with advanced sensors and able to store all that monitoring information, and seeing more frequent use of multivariate statistics and advances in handling of large data sets/machine learning, etc., the questions posed moved away from regular process engineering and into the realm of ‘inverse’ or ‘reverse’ or ‘forensic’ engineering. Customers of the large resin producers were not satisfied by simply getting a resin and then modifying it/post-processing it, but started asking more difficult questions: ‘If I get a polymer resin, then I would like the polymer microstructure you impart in the reactor to give me (to be translated into) desirable final application properties’. Structure-property relationships (SPR) became the name of the game. With process engineering perceived as quite mature, the interest shifted towards product quality.

From the mid-1990s to nowadays (current academic research and industrial interests), and concurrent advances in materials science/nanotechnology, new specialty products came into the fore, a wide spectrum of small/medium industries emerged, and use of computer simulation packages in aid of number-crunching proliferated. In fact, with all modern advances in information technology, the interest in determining product quality, characterizing a product in a more detailed manner (involving such diverse areas as rheology, micro- and nano-reactor technology, 'lab-on-a-chip' approaches, microscopy, etc.), in other words obtaining more precise product properties, became the new focus. The duality/commonality between seemingly different processes is much better understood today. Interfaces are becoming 'blurred' and not as well defined as 30-50 years ago. Scientists are interested in all types of scales. The same analysis and simulation tools (from mathematics and statistics) can help a wide spectrum of processes and products. Polymeric materials research can be applied to and help tremendously (again, seemingly unrelated) areas such as cosmetics, medicine and health applications, bio-medical engineering, biological processes, drug release, materials for optometry, environmental and energy systems, etc.

After many years of interest and successes in polymerization process productivity, we had another 30-40 years of interest (and successes) in polymer product quality. In the last 20 years or so, interest in polymer product quality has morphed into polymer product design. (This is true more or less in all areas of engineering.) The basic milestones in the evolution of polymer research (polymer science/engineering) in both academia and industry (as described above) are summarized pictorially in Figure 1 for quick reference.

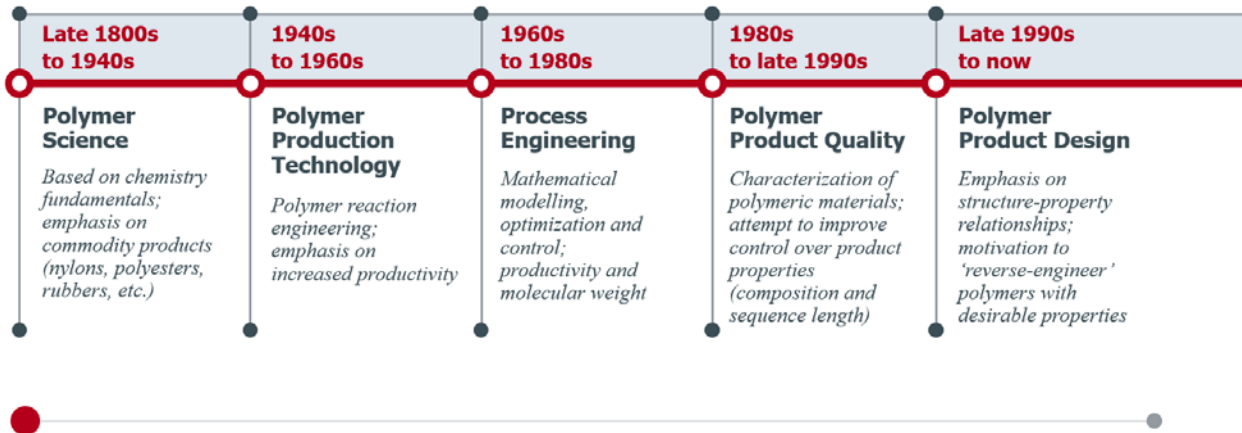


Figure 1: Evolution of polymer research

This has also been the experience with consulting and other industrial projects or contracts. In the 1970s and until the mid- to late 1990s, the questions were around clarification of polymerization kinetics, mathematical modelling and optimization of reactor operation, and attempts at controlling reactor polymer profiles over a pre-specified trajectory. After the mid-1990s, the questions became the opposite. ‘If I tell you what final application (physical, chemical, mechanical, rheological) properties (final behaviour) I want in the final product, if I cite the desirable final performance properties, could you tell me what I should do in the polymerization process, so I obtain a certain desirable spectrum of polymer microstructural properties, which will eventually deliver the desirable application properties?’ And more recently, ‘can I use rheological or mechanical property indicators to design a desirable polymer molecule and hence inform the polymer production people with respect to how to run the reactor?’ In other words, we saw the same shift from process engineering (1960s-1990s) to product design (last 20-25 years).

The senior author of this article has had a long and varied experience in academic research and parallel industrial interactions. The first 20 or so years were on polymer reaction engineering aspects, including multicomponent polymerization kinetics, mathematical modelling of polymerization process, reactor optimization and model-based control, and on- and off-line sensor development for polymer properties (reactor environment and polymer-specific properties). All of these tools (under Polymer Reaction Engineering) helped to shed more light on reactor/process microstructural properties (i.e., molecular properties of the polymer chains as formed inside the

polymerization reactor). This became a very well-informed launching pad for concentrating, in the last 20 years or so, on polymeric product quality and product design. More and more frequently, the questions concentrated on structure-property relationships. The articles by Penlidis and co-workers^[1-11] are very representative of the approaches before and after the mid-1990s, respectively, hence they are representative of the shift described above (in both polymerization and other areas of reaction engineering).

So then, what is polymer product design related to? It is related to imparting desirable properties to a polymer product for specific targets in its behaviour (physical, chemical, mechanical, rheological, etc.) and hence for specific applications. It is intimately related to having a good grasp of meaningful structure-property relationships (SPR). SPRs, in their turn, are related to how meaningful the product characterization indicators/metrics may be, which leads back to microstructural characteristics of the polymeric chains (as formed in the process/reactor), which in turn takes one back to how adequate and reliable one's understanding is of polymerization kinetics and polymer chemistry/science fundamentals. The above steps and the categories they represent are defined in a rather broad sense. For instance, SPRs are representing macroscopic properties and they may involve rheology and post-processing/polymer modification steps; whereas property microstructural trajectories in a reactor involve polymer characterization, monitoring/sensing/detection, parameter and state estimation/filtering, and many other aspects of mathematical modelling and optimization techniques (numerical methods, computer simulation, and database development for polymeric material properties, among others).

The best way to illustrate the above is with examples/case studies. After these examples (Sections 2.1 to 2.3), we will provide a brief summary of takeaway points (Section 2.4), based on this general discussion. Subsequently (in Section 3), more light will be shed on the 'design' of polymeric materials with tailorable properties. We will conclude with two more, recent and long-term, case studies (Section 4). With these final case studies of the paper, the reader will hopefully form a better appreciation of the time- and effort-scales involved, along with the diverse technical background required to accomplish such design scenarios, in order to bring polymeric products from the synthesis stage to the 'fruition' (application) stage.

2.1 Example 1: Methodologies for Obtaining Reliable Indicators for the Environmental Stress Cracking Resistance of Polyethylene

This case study is based on the PhD thesis by Sardashti (2014).^[12] But is it really only one isolated, one-shot, PhD thesis? The answer is no. In fact, in order to reach the culmination of the structure-property relationships (SPRs) obtained in Sardashti's PhD thesis, there were two other PhD theses and three more MASc theses that preceded the Sardashti one. These complementary theses that paved the way were: the PhD thesis by Cheng (2008)^[13]; the PhD thesis by Alvarado-Contreras (2007)^[14]; the MASc thesis by Liu (2007)^[15]; the MASc thesis by Behjat (2009)^[16]; and the MASc thesis by Charbonneau (2011).^[17] In order to reach the meaningful results achieved by Sardashti and described circa 2014/2015, preparatory research and development work started circa 2003. Other characteristics include: (a) The effort was collaborative between Civil Engineering, Chemical Engineering and the Institute for Polymer Research (IPR). (b) It involved collaboration and complementary technical backgrounds by experts in materials, structural mechanics of solids, microscopic and macroscopic structures, polymeric properties, polymer characterization, mechanical properties, and rheological properties. The final application target for the research was polyethylene pipes; to achieve the target, multidisciplinary research and collaboration between experts in polymer science and engineering, polymer melt rheology and mechanical/tensile material properties was required. (c) The expertise traversed fundamental and applied phases, from mathematical modelling all the way to devising practical prescriptions for industrial or ASTM-type materials testing. (d) The effort involved academic and industrial collaboration. (e) The trigger was a combination of modern needs in municipality work on pipe remediation and trenchless technology, and a networking opportunity by the then VP-Research of the University of Waterloo. (f) The research could not have been pursued (i.e., meaningful results could not have been obtained) if the researchers had worked on their own in their own (inevitably narrower) areas of expertise and approach. (g) The effort started from a fundamental question and ended up with very practical 'troubleshooting' tips. (h) The effort showed unambiguously and in detailed steps how to go from basic knowledge (of materials, in the specific case) to property 'operational maps' involving SPRs.

Environmental stress cracking (ESC) is a significant concern in the design and production of polyethylene (PE) products. Therefore, determination of environmental stress cracking resistance (ESCR) is an important consideration for resin producers, plastics processors and end-users. The primary objectives of the whole concerted effort from 2003 to 2015, and more specifically of the doctoral research by Sardashti (2014), were to identify, quantify, and improve the ESCR of PE resins. Several related experimental studies pursued detailed characterization of molecular properties, extensional rheology testing (for both solid and melt states), and the effect of temperature on crystalline phase properties during processing and post-processing. Additional research led to the development of reactive extrusion techniques that could (in principle) enhance the ESCR of polyethylene through long chain branching (LCB).

For the first time in the literature, practical and reproducible standard characterization techniques were designed and developed to predict and quantify the cracking resistance behaviour of polyethylene. Early research sought relationships between molecular structure characteristics and material responses (primarily inter-lamellar entanglements and strain hardening behaviour of PE resins).^[12] Since inter-lamellar entanglements are believed to be the main factor controlling ESCR in PE, extent of entanglements and entanglement efficiency were evaluated using mechanical and rheological experiments. Strain hardening behaviour of PE resins in the solid state was evaluated through a uniaxial tensile test, and PE in the melt state was characterized using extensional rheometry.

First, a standard tensile specimen was designed and a uniaxial tensile test for relative ESCR measurements was developed. Both the specimen and the characterization procedure were developed by rigorous design of experiments and statistical analyses. The newly developed characterization procedure led to the introduction of a new quantifying factor, the “corrected hardening stiffness (cHS)”; this factor can easily be used to rank the ESCR of PE resins with different molecular and structural properties (in a relative way). The novelty of this characterization technique is the reliable and consistent analysis of ESCR without the drawbacks of the conventional techniques (including the presence of aggressive fluids and the subjectivity of the traditional notching process). Also, through this investigation, a reliable standard correlation was established between ESCR and cHS, which makes it possible to estimate a PE sample’s

resistance to fracture, in units of time. This correlation was established based on a variety of PE samples including linear low density PE (LLDPE), high density PE (HDPE), and pipe grade PE resins. Many widely accepted analysis techniques have a degree of subjectivity, whereas cHS seems to be general, reliable, and universally applicable for ranking and/or selecting PE resins.^[18-31]

Second, melt state studies were performed via shear and extensional rheometry. Through shear rheometry studies, it was found that a molecular weight-normalized average characteristic relaxation time can efficiently predict the extent of chain entanglements in resins. This relationship provided a potential melt indicator for a relative measure of ESCR. Through extensional rheometry studies, an inverse correlation was obtained between ESCR and the melt strain hardening coefficient (MSHC) (measured using Sentmanat Extensional Rheometry (SER)). These results indicated that an inverse relationship exists between ESCR and chain extensibility in the melt. Additionally, for the first time in the literature, a new factor called “melt hardening stiffness (mHS)” was developed from the slope of a stress-strain line (obtained from SER). This factor, analogous to cHS, can be used to rank the ESCR of PEs in a practical and reliable manner.^[32,33]

ESCR is typically linked to classical crystalline phase property indicators (i.e., crystallinity, lamella thickness, lamella area, etc.). As such, the third stage of this study focused on the effects of processing and post-processing temperature on the extent of inter-lamellar entanglements. These effects were investigated, evaluated, and eventually correlated to ESCR. Also, since lamella surface area (LSA) is a precise reflection of changes in phase interconnectivity, LSA analysis was pursued. This part of the study focused on the effect of temperature on LSA; the goal was to identify the optimum processing and post-processing conditions which would yield a higher LSA. It was reasonable to assume that PEs with larger lamella lateral surface areas would have more inter-lamellar entanglements, resulting in higher ESCR. In addition, several correlations were developed to address the ambiguity in the literature between ESCR, crystallinity, lamella thickness and lamella lateral area.

Finally, an ultraviolet (UV) photoinitiated reactive extrusion (REX) process was developed so that long chain branches could be selectively formed within the PE structure. Long chain branching

can impose restrictions against stretching of the polymer chain, which consequently enhanced ESCR. This modification resulted in a remarkable fourfold increase in ESCR, which was achieved with very little polymer degradation or crosslinking.^[32]

Ultimately, the PhD thesis^[12] suggested a set of prescriptions that can be used to relate micro-molecular chain indicators (defined in the reactor during production) with mechanical/tensile properties of PE including ESCR. The goal was to relate an empirical and unreliable indicator (ESCR) to a more precise and reliable fundamental property (hardening stiffness, from a stress-strain test). In the near future, it will be possible to replace existing tests (currently in use as a standard (via ASTM or ISO)) with another test that will be more reliable and material-independent.

Figure 2 and Figure 3 provide a quick summary of the above discussion. Figure 2 demonstrates examples of the mechanical and rheological testing that led to new indicators for evaluating ESCR of different polyethylene resins; descriptions of characteristics found in axes' labels and legends can be found in the original work^[12] and related publications. In Figure 3, different property 'operational maps' are exemplified, relating important PE properties including density, molecular weight (where MW in the figure refers to weight-average molecular weight of the resins), crystallinity and ESCR. In theory, these maps make it possible to select the appropriate polyethylene resin(s) for a specific target application. At the same time, one can rank a resin with unknown properties based on some of the possible indicators (and without having to go through each testing stage). More information and details can be found in the PhD and MASc theses and the numerous publications that resulted therefrom (cited earlier).

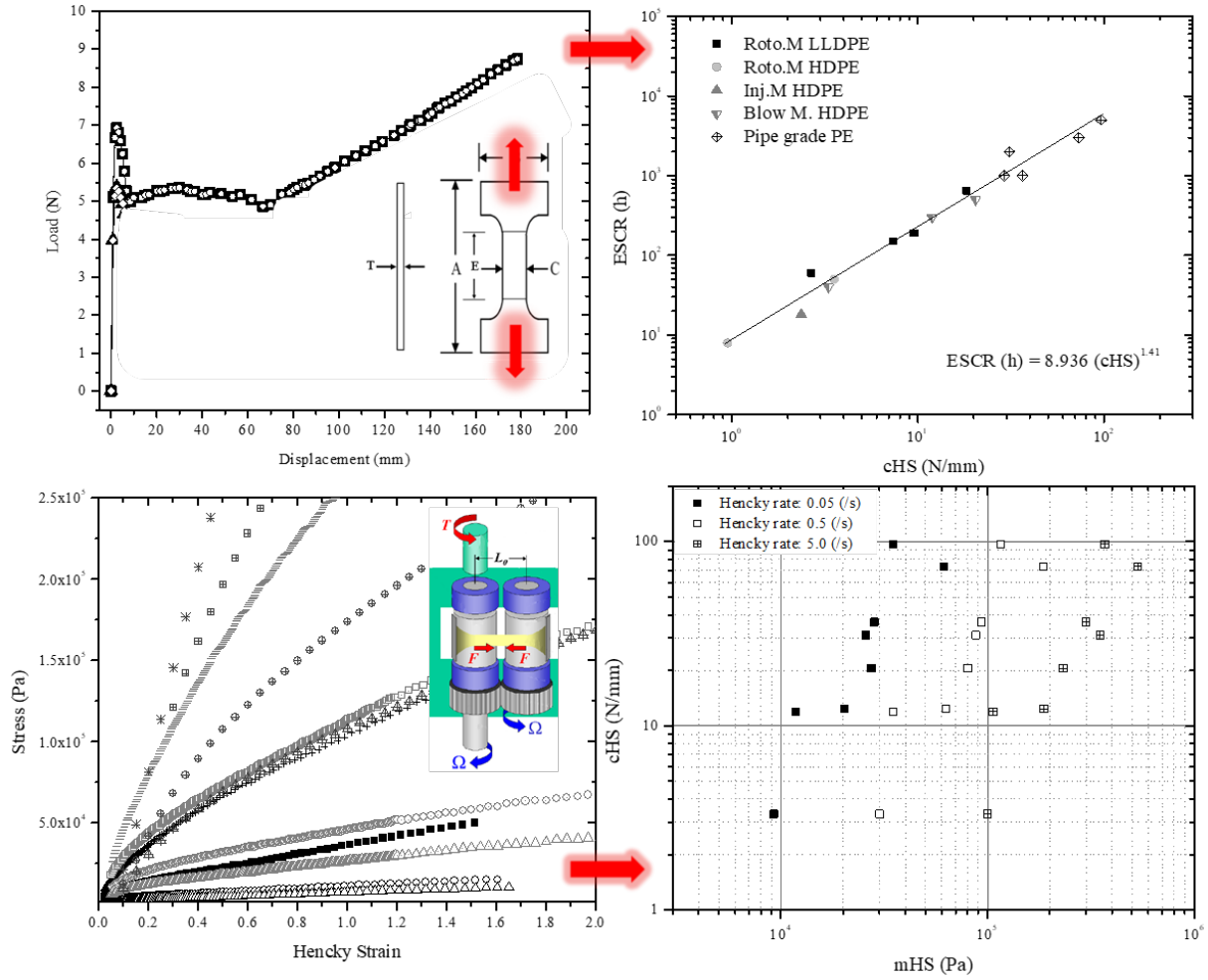


Figure 2: Mechanical (tensile strain hardening) testing and rheological (SER) testing to identify reliable indicators of environmental stress cracking resistance of polyethylene^[12]

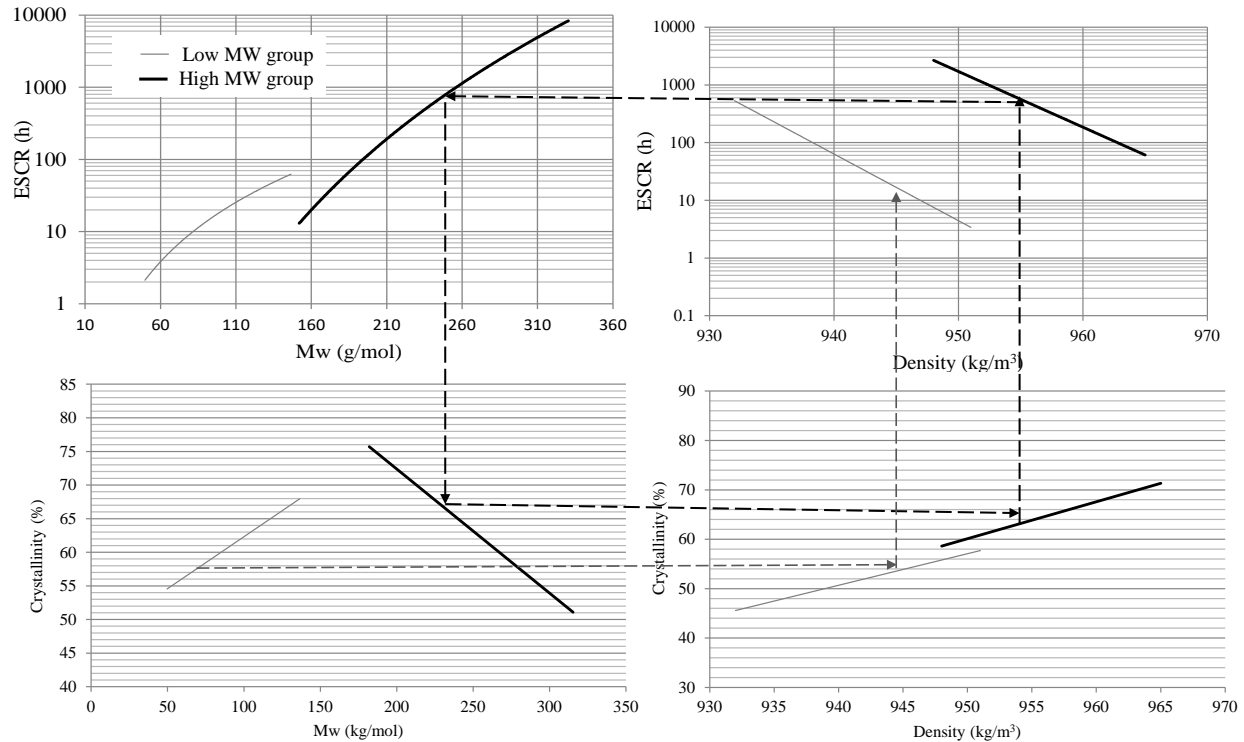


Figure 3: Property maps to relate environmental stress cracking resistance to structural properties of a variety of polyethylene resins^[34]

2.2 Example 2: Rheological Modification of Polypropylene by Imparting Long Chain Branches Using UV Radiation

This case study is based on the PhD thesis by Amintowlieh (2014).^[35] Of course, some key words, some technical terms and names will change, but the considerations, development history, and characteristics are the same as the ones described above in the first paragraph of Section 2.1. The related time-frame that eventually led to Amintowlieh's results (including a US patent) may have easily spanned research efforts over 15 years.

Polypropylene (PP) is one of the most common thermoplastics; the wide variety of PP applications includes household appliances and automotive interiors. Each unique application requires a specific PP grade with a distinct molecular structure, molecular weight (MW) and molecular weight distribution (MWD). PP molecular weight and polydispersity index (PDI) can affect the melt flow behaviour, the processing characteristics and, eventually, the final application performance. Besides, PP has low melt strength and, consequently, it has limited use when higher

melt strength levels are required (consider, for example, blow moulding, extrusion coating, fibre spinning, foaming, and thermoforming). Melt strength can be increased through the incorporation of long chain branches (LCBs) into the PP backbone. When long chain branching occurs, entanglements of polymer chains and interactions between polymer chains are more likely to take place. Thus, the polymer becomes more resistant to extensional deformation in the melt state (that is, the melt strength increases). As such, there is motivation to establish versatile techniques to adjust the PP molecular structure for different applications and processes. In addition to forming special structures such as LCBs or crosslinks (CLs) via post-polymerization modification techniques, narrowing the MWD of PPs via degradation and β -scission (controlled rheology PP) may also be of interest.

To introduce LCBs to the polymer backbone, a tertiary hydrogen must first be abstracted from said backbone. Free radicals, which can be generated via peroxide initiator decomposition or high energy radiation (i.e., electron beam (EB) or gamma radiation), are often used to achieve the initial hydrogen abstraction. Then, when a tertiary radical center combines with another radical center, branches form on the PP backbone. The primary challenge during this process is the tendency of PP macroradicals to degrade via β -scission followed by termination via disproportionation (formation of controlled rheology PP).

Despite recent advances in PP modification, there are several disadvantages associated with the most widely used techniques. Peroxides, for instance, introduce toxicity concerns. Additionally, EB and gamma radiation are expensive energy sources and require unique safety considerations. In contrast, UV radiation is an easily accessible (and a relatively inexpensive) energy source; photoinitiators such as benzophenone (BPH) have been used for modification with UV radiation. BPH and other similar photoinitiators absorb UV energy to produce free radicals; the process of modifying PP using a photoinitiator and UV radiation is referred to as photomodification. Generally speaking, photoinitiators are promising modification agents because they are less toxic than peroxides and can be activated by UV radiation rather than thermal energy. Also, controlling photoinitiation reactions is easier than controlling peroxide-induced thermal initiation, as there are more opportunities to adjust temperature without unintentionally activating the (thermal) initiator.

In the PhD research by Amintowlieh (2014)^[35], UV photomodification (that is, a photoinitiator activated by UV radiation) was employed to abstract hydrogens from PP backbones and to initiate polymer modification. The reaction was conducted in the solid state. Ultimately, the final PP molecular structure depended on the concentration of the photoinitiator, the amount of time the material was exposed to radiation, the intensity of the UV lamp, the temperature of the radiation and the type of photoinitiator that was used for modification.

An optimal design of experiments was utilized to identify combinations of these variables that resulted in degraded, long chain branched PP with improved melt strength or crosslinked PP. In order to characterize the molecular structure of PP, rheological measurements were found to be versatile and reliable tools. Rheological techniques, along with gel permeation chromatography (GPC) and gel extraction, were adopted to obtain processing/property maps for specific molecular structures in PP. Details such as number of long chain branches (LCBs), percentage of gel, and strain hardening behaviour of long chain branched PP versus the molecular structure of degraded PP were compared using these characterization techniques. After detailed analysis of the effects of different radiation variables on PP modification, the optimal range of photoinitiator concentration, UV lamp intensity, and radiation temperature to form LCBs in PP was determined. It was also clarified that radiation time required to form long chain branched PP (rather than degraded PP) depended on the thickness of the PP sample.

One of the main challenges in using UV photomodification is the limited penetration depth of UV. To systematically investigate the effects of UV penetration depth and radiation time, discs of different thicknesses were made and radiated for various durations. Experimental results indicated that as sample thickness decreased and/or radiation time increased, more LCBs were formed. In an additional investigation, the UV penetration depth in PP solid samples was also evaluated for specific lamp intensity. It was found that long radiation times (> 5 minutes) were required to produce long chain branched PP at a thickness above 1 mm; this would limit the potential to use this technique in commercial applications. Therefore, to try and reduce the required radiation time, a coagent (trimethylolpropane triacrylate, TMPTA) was added to the formulation. TMPTA is a trifunctional acrylic monomer, and was used as a coagent to stabilize the radical center and reduce polymer degradation. Utilizing statistical/optimization tools again, optimized combinations of

coagent concentration, BPH concentration and radiation time were identified to produce long chain branched PP (with minimum gel content) or crosslinked PP. Rheological measurements such as relaxation spectra analysis, GPC and gel extraction methods were utilized to characterize and compare different structures of PP upon photomodification.^[36-38]

Finally, and in order to pursue scale-up potential of PP photomodification (and its eventual commercialization), the typical process design was modified and a method for the continuous radiation of PP was developed. The design included photomodification of solidified strands of PP after extrusion from a twin-screw extruder. Each strand was stretched and folded several times over two parallel rollers. Strands stretched between rollers were exposed to UV radiation, and then the radiated PP strands were collected on a winder. This continuous photomodification was successful in forming various PP grades both with and without coagent. Once again, practical processing (operational) ‘maps’ were constructed to shed more light on the topology and sensitivity/feasibility of the optimum point, and to guide the continuous production of both long chain branched PP or crosslinked PP with various MW and MWD properties.

In general, the results obtained over this long experimentation phase have demonstrated that UV radiation can be used to modify PP and to form different grades of PP, ranging from controlled rheology PP to long chain branched and crosslinked PP. We not only identified the significant factors during PP photomodification, but also optimized these variables to form various desirable PP grades, hence contributing to faster product design. An additional bonus of the systematic design approach was that this process could be scaled up from bench scale to commercial scale.^[39,40]

2.3 Other Examples

These additional research examples will be cited very briefly for the interested reader.

The first group is related to crosslinked network heterogeneity (or homogeneity) indicators, comparing free radical (regular) (co)polymerizations with controlled radical (co)polymerizations, all producing networks (crosslinked material). The interested reader can get a very good flavor of

the different aspects and considerations involved from several papers^[3,4,41-43] dealing with the nitroxide-mediated radical copolymerization of styrene (sty)/divinyl benzene (DVB); and from work by Perez-Salinas et al.^[44] dealing with the reversible-addition fragmentation copolymerization of 2-hydroxyethylene methacrylate (HEMA)/ethylene glycol dimethacrylate (EGDMA), including synthesis under supercritical carbon dioxide conditions.

The second case is related to the design of a processing aid in order to improve processing and surface properties of linear low density PE (LLDPE).^[45]

2.4 Takeaway Points for Arriving at Meaningful SPRs and Polymeric Material Design

Interspersed within the statements of the previous examples described above, here is a list of typical characteristics needed, common to all these complex research studies: (a) About 10-15 years of research. (b) Collaborative and concerted long-term efforts that take more than just a phone call or a chat in academia's corridors or a mention in one's CV! (c) Collaboration and complementary technical backgrounds by experts in materials, structural mechanics of solids, microscopic and macroscopic structures, polymeric properties, polymer characterization, mechanical properties, and rheological properties. (d) Fundamental and applied phases, from mathematical modelling all the way to devising practical prescriptions for industrial materials testing. (e) Academic and industrial collaboration. (f) Administrative people and managers who are there to facilitate research and collection of results. (g) The different parties involved should realize from the outset that the research cannot be pursued (i.e., meaningful results cannot be obtained) if the researchers work on their own in their own (inevitably narrower) areas of expertise. (h) The efforts may start from either a fundamental or applied question. (i) A funding manager or administrator should have no illusions that such efforts may offer resolutions or solve a problem in 18-24 months! (j) Although this can be perceived as a repeated platitude, as it is the first item that somebody has to set in any investigation, clear objectives/targets are indeed required. In many a case, this has created issues right from the outset. For instance, a few years ago, a company approached us and asked us to help them develop SPRs. When we asked 'SPRs on what?', we were faced with silence. It makes a difference if the SPRs are for polyethylene or polyvinyl chloride or nylon (materials with good background information) vs say, new terpolymers used in

organic electronics or new materials for coating technologies or new sensors in smart food packaging technology. (This also happens often in optimization studies, when one assumes that the researcher has already defined an objective function to be optimized; upon further scrutiny, one may realize that the objective function is rather vaguely expressed.)

3. BREAKING DOWN THE DESIGN APPROACH

The examples described so far demonstrate the success that can be achieved when researchers take the time to pursue an interesting question based on good understanding of polymer synthesis and/or modification procedures, structure-property relationships, and application requirements. This background has motivated the need for a more structured (yet still versatile) design approach for the selection, synthesis and subsequent characterization (and testing/evaluation/ranking) of polymeric materials for a targeted application. In the PhD thesis by Scott (2019)^[46], a design framework was developed based on accumulated experience from these long-term investigations described previously, and on more recent case studies (to be described in more detail in Section 4). This systematic framework is aligned with ‘best practices’ for general material (emphasis on metals) design efforts (see, for example, these sources^[47,48]).

3.1 Design Framework

The design framework developed (and tested) contains three related stages. The first stage (described in Section 3.2) requires a good understanding of product requirements. The middle stage (described in Section 3.3) allows for an improved awareness of product customization and provides an opportunity for preliminary characterization. Relationships between polymer formulations, structures and properties cannot be manipulated if they are not first well-understood! The final stage (described in Section 3.4) moves us towards optimally designed materials, characterizes the most important properties, and still allows for modifications (as needed) to meet the desired specifications. A key aspect of this framework is the sequential and iterative nature of design: the characteristics of the polymer products (either in the preliminary investigation or in the optimal synthesis step) may not always meet the target requirements. In these cases, designing new

screening experiments (with different polymer backbones, different customization techniques, etc.) may be the most appropriate path forward in this iterative optimal scenario.

One could add several specific examples of the different stages of the iterative scheme. A more specific example is discussed later in Section 4.1.3. However, there are also more general examples of this iterative scheme. For instance, one can start an investigation with a few polymeric resins. After the first stages of data collection, one may realize that the selected resins do not cover the whole gamut of properties or options, based on possible applications. In such a case, one may add new resins/polymeric materials or synthesize new ones or modify other existing ones. The current paper has examples of all of the above. On the other hand, one may drop a resin from the investigation, if the data collection shows that several of the selected resins are very similar and hence do not offer a wide spectrum of properties or structures. In another example, one may start, say, with three different testing procedures (three different tests, three different pieces of equipment (that try to evaluate the same property indicator), or three modifications of a technique). One may observe at the next stage of the investigation that one technique is overly noisy, but two are in good agreement. The noisy technique may be dropped as unreliable. One may also add a new testing procedure, if the literature or experience (academic or industrial) reveal such a new and relevant technique.

These are all examples of viable changes during the iterative scheme. Of course, many structure-property investigations are case-specific, so we would not like to belabour the point with generalities or restrict the discussion with specifics. The investigator is free to go back and question results at any point, depending on the degree of achievement/completion of the final targets of the investigation.

Two case studies were used to develop (and eventually demonstrate) the design framework described herein. The first case study (described further in Section 4.1) involved the selection, design, synthesis and characterization of polymeric sensing materials for the detection of various gas analytes. Formaldehyde or benzene detection may be useful for indoor air quality analysis, ethanol detection may be used for prevention of impaired driving, and acetone detection has potential biomedical applications. The second case study (described further in Section 4.2)

examined the improvement of synthetic water-soluble polymers for enhanced oil recovery (EOR) polymer flooding. In many cases, polymers for EOR are exposed to high temperatures, high shear rates, and high concentrations of salt in the reservoir. The shortcomings of typically used materials include poor thermal stability, poor shear stability, and poor brine compatibility. As a result, polymeric materials can degrade during EOR, thus lowering molecular weight averages and reducing oil recovery efficiency. Therefore, the target for this case study was to build on existing knowledge to improve synthetic polymers for enhanced oil recovery.

These distinct (yet related) case studies were selected to highlight the fact that a design approach is not limited to a particular industry or application, nor to a specific type of polymeric material. The case studies both use the same general design framework in a sequential, iterative manner to move towards optimally designed materials for each target application.

The general framework developed in the PhD thesis by Scott^[46] is shown in Figure 4; the approach is intentionally very general, which ensures that it can be applicable to a wide range of polymeric materials and related applications. This can essentially be used as a ‘road map’ for the design of polymeric materials, which can help researchers to clarify the investigation steps (and sometimes omit them altogether, if not needed or if the specific background knowledge already exists) and to draw links between different stages of a given project. Specific stages of the design framework are described in more detail in the following sections.

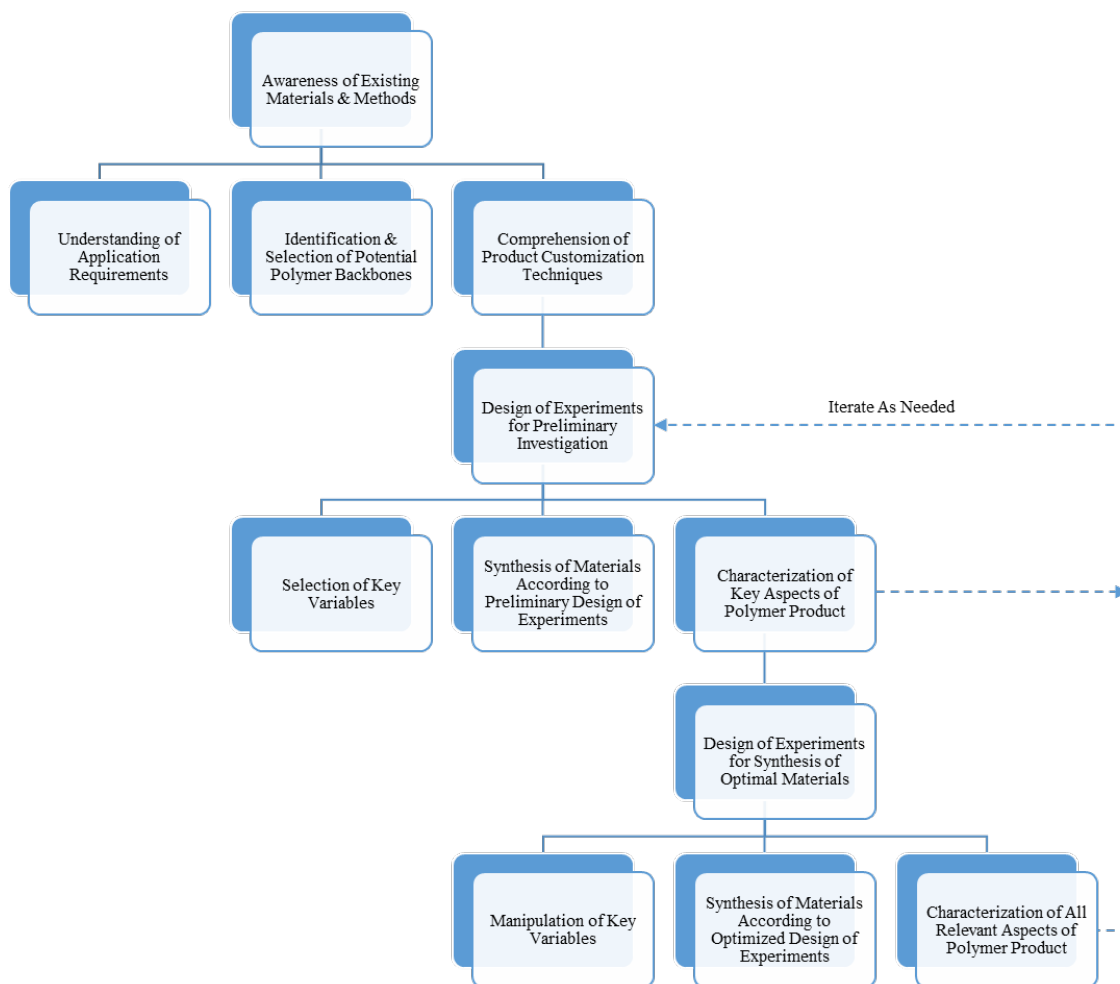


Figure 4: General framework for the design of polymeric materials for custom applications^[46]

3.2 Awareness of Existing Materials and Methods

Before undertaking any new investigation, it is important to identify (and build upon) prior research in the area. This may seem obvious, but it can be tempting to initiate a new project without a full understanding of existing materials and methods used for the application. (This may be observed to happen every 25-40 years, as ‘research’ - or ‘institutional’-memory may be lost.) The importance of prior knowledge in design cannot be understated; existing work (done either by the current researcher or by other research groups) should always be critically examined and used as a building block for new studies. Although such strictures may sound like platitudes, the discipline

involved in considering/thinking through the purpose of the background of an experimental program is very valuable. If the program involves collaboration, time used in building up knowledge and subsequently clarifying the main objectives is always well spent, and the effort is very informative.

Ashby and Johnson^[47] describe four selection methods for material design: analysis, synthesis, similarity and inspiration. Typically, at least one of these selection methods is applicable to the design of a new material. That said, research (like thinking) is rarely limited to a single selection method. In fact, several different methods can be used simultaneously to increase the information available for design. A brief overview of the four selection methods is provided herein, and more details are available in the original work.^[47]

Selection by *analysis* is primarily motivated by an understanding of the technical requirements for an application. The general principle is to translate the (often non-technical) requirements into a statement of objectives and constraints, analyze and identify important material properties (those that determine performance), and screen a database of materials and their properties (this makes use of existing materials and methods). During the screening process, any materials that do not meet the constraints can be eliminated, and those that remain can be evaluated in terms of anticipated performance. Selection by *synthesis* takes advantage of prior knowledge and essentially combines desirable properties from several existing technologies. New solutions (that is, new polymeric materials) can be developed by examining materials with desirable features and incorporating those materials (and, therefore, those features) into the new product.

Selection by *similarity* is exactly as the name suggests: building from existing (or potential) solutions for a given application. This technique is typically used when an established material becomes unavailable or shows room for improvement in one or more aspect. Of course, the new material should have similar properties to the existing (currently used) material, except in the aspect where we are targeting improvement. Finally, selection by *inspiration* is arguably the least technical approach; it relies on creative thinking and exploring ideas somewhat randomly.^[47] Although the selection of materials by inspiration does not rely as heavily on the design principles described previously, it is important to leave some room for creativity in the process of designing

new materials. In this case, flexibility is important, and an element of luck is intimately involved in successful applications.

Regardless of the primary selection technique employed, all selection methods require databases of materials, methods and products (or at least a good understanding of current best practices). This is especially critical to aid in the understanding of specific application requirements. As evidenced in the earlier examples (Sections 2.1 and 2.2), most microstructural and bulk polymer properties are intrinsically related to the application performance. A good understanding of these requirements (both for the material itself and for the end-use application) allows for informed (targeted) selection of potential polymer backbones.

Identifying promising polymer backbones for a given application can require a significant amount of exploration. As described already, researchers can make use of analysis, synthesis, similarity, or inspiration during this design stage. However, for any of these approaches, some prior work (or databases, if available) must be referenced so that the researcher can become familiar with the relevant properties of each candidate backbone. Again, this highlights the importance of having a solid background (both technical and of the prior work): here, the goal is to combine information about existing materials and methods, knowledge of product requirements, and relevant data for polymeric materials to create a ‘short-list’ of potential polymers for the target application.

Finally, comprehension of product customization techniques can be extremely beneficial for design. Since new materials are (typically) being developed, the possibility to customize said materials is largely based on theoretical knowledge. For example, one might be aware of the potential effects of reaction conditions on a particular type of system, but data may not yet exist for the exact system being considered; in such cases, preliminary (screening) experimental work may be required. Determining the effectiveness of specific polymer backbones (with the related main or side functional groups) and product customization requires moving from theory to practice.

3.3 Design of Preliminary Experiments

The main purpose of a preliminary (exploratory, screening) experimental investigation is to establish relationships between key variables and the most relevant polymer properties. This is accomplished using statistically designed experiments, which makes it possible to obtain the most experimental information in the fewest experimental runs (that is, making the best use of resources). Even in preliminary investigations, careful experimental replication is critical. This provides a measure of the reproducibility/repeatability of the collected data and ensures that the relationships identified are legitimate. The replication step is often overlooked in the literature, but it is crucial at each stage of any investigation.

Once the main factors (variables) are identified and the design of experiments is developed, we move to polymer synthesis and characterization. It is important to note that the characterization at this stage is specifically for *key* polymer properties. That is, not all conceivable (relevant) polymer properties are investigated during the preliminary investigation. Carefully selected characteristics (whether related to polymer properties or application performance) can give us an indication of whether or not the material seems promising for the target application. Also, characterization results can provide some insight on how to further improve the material(s).

Typically, characterization methods employed at this stage should not be overly expensive or time-consuming. In an ideal world, testing the key polymer properties should only require small quantities of polymeric material (that is, large batches of preliminary polymer samples should not be required, again retaining valuable resources). It is also helpful if the preliminary characterization steps are relatively uncomplicated, especially if they can be done ‘in-house’. Here, researchers should be looking for an overview of the materials’ performance. The results from this stage (along with additional background information from the literature or from experience) can assist in identifying the most promising materials and in discerning the most important variables. This ultimately leads to the synthesis of more customized materials.

3.4 Design of Optimal Materials

The results obtained from the preliminary experiments inform the design of optimal materials. At this stage of the design process, we have already identified key variables (and their impact on

polymer properties) from the preliminary runs, so we can select new formulations that are expected to have desirable properties. The optimal design stage may be the final stage of the investigation, but it is also possible that some ‘fine-tuning’ will be needed. Therefore, the design cycle can be reiterated as needed, until the application requirements are met. Using sequential and iterative procedures leads to optimality.

The final aspect in the design of optimal materials is to evaluate (test) all relevant characteristics of the polymer products. This will likely include re-evaluation of ‘key’ characteristics measured in the preliminary stage as well as the evaluation of new properties that are essential for application performance. Typically, optimally designed polymeric materials should be evaluated in greater detail than those synthesized in the preliminary study. Since this is (often) the final stage, it is important that we know as much as possible about a given material. For example, do material properties match with model predictions? Do the materials perform well for the desired application? Do the materials perform well within the typical operating regions? Do materials behave better than the (currently available) reference material in the areas we claimed? Could one extrapolate to different operation regions, and if yes, how successful are the new or modified materials? Sometimes, answering these questions can involve more time-consuming (and more costly) experimental work, so the full evaluation is reserved for the samples that we have designed (and, ultimately, the materials in which we are most confident based on their properties). This again saves money, time/effort and resources, in contrast to the typically employed trial-and-error (or other arbitrary) approaches. Whichever properties are evaluated should be relevant to the target application and should supplement the available information about the materials. Eventually, these characteristics may even be used as prior knowledge for future (fine-tuning) studies targeting new applications (or improved modified materials).

3.5 Applying the Design Framework

The design framework described herein (and illustrated in Figure 4) can be applied to any novel polymeric material; two case studies are presented in Section 4. Beyond these two case studies, many more opportunities exist for optimization. This design approach (along with the previously cited examples and related references) is intended to act as a general framework, which should

encourage researchers to make use of prior knowledge, carefully designed experiments and targeted analysis to make the most of their resources. Ultimately, using sequential and iterative techniques makes it possible to converge on an optimally designed material for a specific target application.

An awareness of existing materials and methods can inform statistically designed preliminary experiments, which eventually lead to optimally designed materials for specific (targeted) applications. The effectiveness of a design framework is visible throughout the research process, but it is especially evident in the application performance of the final (optimal) product, along with the flexibility of the design approach with respect to expanding into new areas, at the same time minimizing time and effort. Essentially, there is nothing more innovative and efficient than following a systematic and consistent plan. (If approaches are inconsistent, they become arbitrary rather quickly.)

4. CASE STUDIES: DEMONSTRATING THE DESIGN FRAMEWORK

In the first case study (Section 4.1), a series of polymeric sensing materials were designed for the detection of various gas analytes. Using a designed approach ensured that target functional groups, solubility parameters, operational temperature, and product customization were considered in the early stages of the investigation. In this case, relevant links were established between the material properties of each polymer and the sensing ability (both in terms of sensitivity and selectivity).

In the second case study (Section 4.2), multi-component polymers were designed for polymer flooding (an enhanced oil recovery technique). Initially, there was significant emphasis on multi-component polymer chain composition (and hence, reactivity ratios, since they describe monomer unit incorporation rate), largely because multi-component systems with unique polyelectrolyte behaviour were selected for the application. Since the application performance (that is, enhanced oil recovery efficiency) was not easily evaluated, many other characteristics were studied first to improve our understanding of the polymeric material properties (microstructural and macroscopic). The characterization of the optimally designed materials provided the confidence necessary to pursue additional (more time-consuming and more resource-intensive) application-

specific testing, namely polymer flooding tests and heavy oil displacement tests, in order to complete the circle.

More details about each case study are provided in what follows.

4.1 Case Study 1: Design of Polymeric Sensing Materials

As described in earlier sections (especially Sections 2.1 and 2.2), the depth of knowledge required to pursue optimally designed polymeric materials takes significant time and effort. As such, designing polymeric sensing materials (the case study described herein) has spanned several MAsc and PhD theses (over about 12 years), starting with those by Stewart (2011, 2016).^[49,50]

Sensing materials can be designed to interact with some target analyte through sorption. The specific mechanisms associated with polymeric sensing materials can be fairly complex, and vary considerably (depending on the polymeric material and the target analyte); more details can be found elsewhere.^[51]

4.1.1 Polymeric Sensing Materials for Formaldehyde Detection

The initial project^[49,52] investigated polymeric sensing materials for the detection of formaldehyde, which would be used for indoor air quality monitoring. Application requirements (including an affinity towards the target analyte, selective detection of the target analyte in the presence of interferences, desirable limits of detection, chemically and thermally stable materials, operational at reasonable temperatures, etc.) were identified early on in the project, and potential polymer backbones were selected. Based on an awareness of existing materials and methods, polyaniline (PANI) was the polymer backbone of choice.

PANI is one of the most widely used sensing materials, largely due to its versatility. In fact, five different oxidation states of PANI exist. Emeraldine is the most stable form, but any form can be obtained through oxidation or reduction reactions (for example, leucoemeraldine is in a fully reduced state, whereas pernigraniline is fully oxidized).^[53] An additional advantage of PANI is

that it can be made conductive by protonic acid doping. Essentially, in an acidic (or salt) form, polyaniline becomes conductive without the addition or removal of electrons. The doped form of PANI can be achieved by modifying the basic (non-conductive) form, or the more common 'self-doping' technique can be performed by adding acid to the pre-polymerization recipe in the synthesis phase.^[54]

PANI has been used to detect several target species including ammonia, benzene, carbon monoxide, chloroform, ethanol, hydrogen, hydrogen sulfide, methanol, nitrogen dioxide, toluene, water and xylene.^[55] While this may seem like it could cause problems with selectivity, it actually demonstrates the versatility of PANI as the main backbone of various tailored sensing materials.

PANI can also be doped with metal oxides or acids to improve sensing properties like sensitivity and selectivity, electrical conductivity, thermal stability and mechanical integrity. The effectiveness of metal oxide dopants depends on several factors. These factors include the degree of incorporation of the metal oxide, potential morphology changes in the polymer's surface structure, potential for metal coordination, and the metal oxide's affinity towards the target analyte.^[56] Ultimately, experimental evaluation is required to establish the effects of metal oxide doping of a specific polymer backbone for a particular target analyte (incidentally, a specialized test set-up was built in our lab for that express purpose^[57]).

In the investigation of polymeric materials for formaldehyde detection, polyaniline (PANI) backbones were doped with varying levels of nickel oxide (NiO) and/or aluminum oxide (Al₂O₃). Varying the dopant levels changed the sorption response significantly, both in terms of sensitivity and selectivity. Eventually, two formulations stood out: PANI doped with 15% NiO had the highest sensitivity towards formaldehyde at very low formaldehyde concentrations (< 1 ppm), and PANI doped with 5% NiO and 15% Al₂O₃ showed promising selectivity towards formaldehyde (at concentrations > 1 ppm but below 5 ppm) in the presence of other interferent gases (including acetaldehyde and benzene).

Based on the results of the formaldehyde sensing material study, the next step^[51,58] involved work of a more fundamental nature, towards developing more general prescriptions for designing

sensing materials. Preliminary prescriptions suggested that the target analyte would dictate the material needed for the sensor. For example, if the analyte is inorganic, then some type of metal oxide would be most suitable as the sensing material. On the other hand, for organic analytes, further classification is required: classification according to functional groups (amines, aromatics, alcohols, aldehydes, etc.) is beneficial. For instance, polarity and hydrogen bonding might be potential mechanisms for alcohol sorption on a particular sensing material, whereas steric hindrance may prevent aromatics from sorbing. At this stage, the potential usefulness of dopants (and metal coordination potential) might also be considered.^[51]

Next, the type of sensor (resistive, conductive, mass-based, etc.) should be identified. Here, it is possible to establish sensor constraints and to continue narrowing down the list of potential sensing materials. As an example, a sensor that functions based on resistance changes would require a conductive sensing material, whereas a mass-based sensor would require a lightweight sensing material. Other factors including detection limit, operating temperature, and potential for sensing material regeneration should also be taken into consideration at this point. Essentially, the sensing material must be able to detect the target analyte at a specified (low) concentration and must be able to do so at an appropriate operating temperature. In most cases, reusable sensors are preferable, so the sensing material selected should be able to be regenerated.

Once all relevant factors have been taken into account, one should have a ‘short-list’ of candidate sensing materials. From there, the list may further be condensed based on processability, cost of materials, or other considerations. The remaining sensing materials can then be tested experimentally to determine which show the most promise.

This approach is somewhat more specific and one can see parallels with what was described in Section 3. In selecting polymeric materials for formaldehyde detection, the first step was to establish an awareness (essentially a database) of existing materials and methods. Understanding application requirements led to the identification and selection of types of sensors and of potential polymer backbones, and product customization techniques (namely doping) were explored. The final step was the experimental investigation and data collection. If those initial results had been

discouraging, it would have been entirely appropriate (and necessary!) to apply an iterative design process.

The same design principles have since been applied to other volatile organic compounds. In each case, one must consider the application requirements (both in terms of polymer properties and application-specific behaviour) and consider appropriate candidates for polymeric sensing materials. Some additional investigations are described in Sections 4.1.2 through 4.1.4.

4.1.2 Polymeric Sensing Materials for Ethanol Detection

The next target analyte on this sensing material journey was ethanol.^[50,56,59] Ethanol detection, either through breath alcohol samples or transdermal measurements, is a motivating target for the reduction of impaired driving. Based on prior knowledge (both from the results of Section 4.1.1 and from the literature), Stewart^[50] investigated potential sensing materials using a targeted design approach.

Initially, the polymeric sensing materials for ethanol detection were chosen based on previous experience and literature. From there, a preliminary set of sensing materials was evaluated (in terms of sorption ability) and then new potential sensing materials were chosen based on the trends observed. It was important to find sensing materials that were both highly sensitive and highly selective to ethanol (in the face of common interferents (other gas analytes present)).

As mentioned earlier, analytes and sensing materials interact through sensing mechanisms.^[51] These sensing mechanisms are based on the chemical nature of both the sensing material and the analyte. If the interactions between polymeric sensing materials and volatile organic compounds (VOCs) are well-understood, they can be exploited for the detection of target analytes. By comparing polymeric sensing materials for multiple VOCs evaluated or presented in the literature, trends were found that suggested specific sensing mechanisms. These trends and sensing mechanisms were evaluated using specifically designed case studies. Based on this additional information, the sensing mechanisms were categorized and organized to produce a set of prescriptions that could be followed when designing new potential sensing materials for a target

analyte. These prescriptions also take into account any other constraints due to the specific sensor application. This approach is a more direct route to designing polymeric sensing materials for a target analyte and sensor application than typically used trial-and-error procedures. General prescriptions are presented in Figure 5, while suggestions and prescriptions for analytes with specific functional groups (including amines, aromatics, alcohols, aldehydes, etc.) have been prepared by Stewart and Penlidis.^[58]

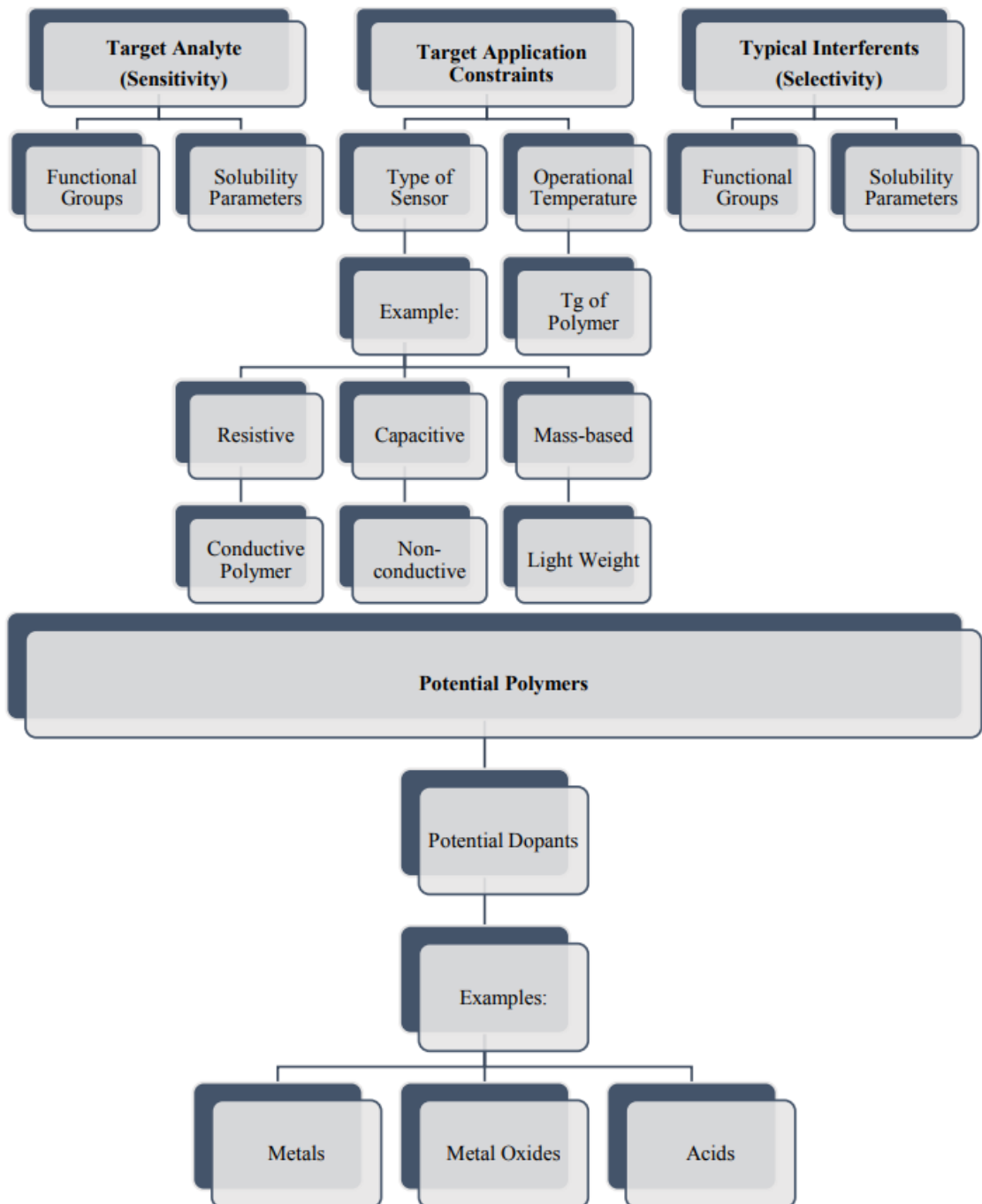


Figure 5: Practical prescriptions for the selection of polymeric sensing materials^[58]

In order to design sensing materials for ethanol detection, specific properties of alcohols can be exploited. Ethanol is polar (that is, the oxygen is more electronegative and the other atoms more electropositive) and is able to hydrogen bond because of the large dipole created between the

oxygen and hydrogen. Therefore, alcohols are attracted to sensing materials that are polar, especially those able to hydrogen bond. An additional technique for selecting a sensing material is to compare the solubility parameter of the target analyte to the solubility parameters of potential sensing materials. Solubility parameters take many material properties into account, which can help predict both solubility and sorption potential. If the solubility parameters for the analyte and the sensing material are close in value, this indicates that the materials are likely to interact.

Polyaniline (PANI), described previously in Section 4.1.1, is a common sensing material for ethanol (see, for example, these works^[60-62]); the polymer backbone contains an amine group that makes it polar and capable of hydrogen bonding (Figure 6a). As described earlier, PANI has the flexibility of being conductive or non-conductive, depending on acid doping and the related charge. Stewart and Penlidis^[58] suggest that positive charges along the polymer backbone (due to acid doping) are able to attract electronegative atoms and molecules (such as ethanol or methanol) because of the larger dipole and therefore, stronger electrostatic forces.

Derivatives of PANI like poly (*o*-anisidine) (PoANI) and poly (2,5-dimethyl aniline) (P25DMA) can also be used as sensing materials. These derivatives maintain many of the desirable sensing characteristics of polyaniline, but also have some improved features like better solubility and processability (due to less dense packing).^[50] A schematic comparing PANI to PoANI and P25DMA is presented in Figure 6.

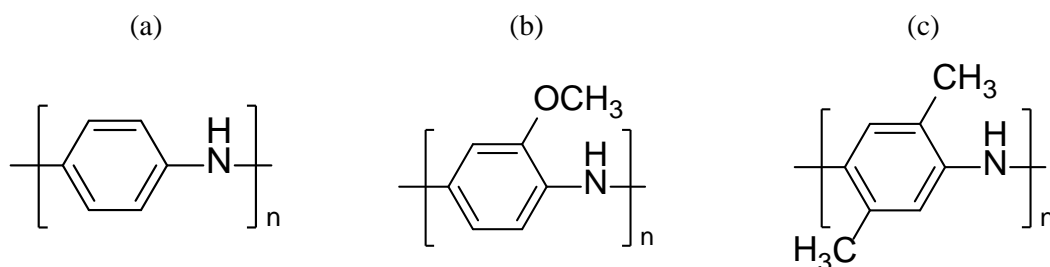


Figure 6: Polyaniline and sample derivatives (a) PANI, (b) PoANI and (c) P25DMA

The targeted search for polymeric sensing materials for ethanol detection involved the evaluation of about fifty (initially), later reduced to over thirty potential sensing materials. The synthesis and characterization of several of the materials is described by Stewart and Penlidis.^[63] Three polymer

backbones (PANI, PoANI and P25DMA) were initially selected, and each was doped with varying concentrations of five different metal oxide nanoparticles (Al_2O_3 , CuO, NiO, TiO_2 , and ZnO). Additional polymer backbones, including specialized siloxane-based polymers and other polymers such as poly (methyl methacrylate) (PMMA) and polypyrrole (PPy) were also considered. The preliminary stage of this project included identifying potential polymer backbones, selecting customization techniques, synthesizing/preparing the polymer sensing materials, and characterizing their sorption ability. From this preliminary stage, the most promising materials were identified (both in terms of sensitivity and selectivity towards ethanol).

Of these thirty plus sensing materials, most were able to sorb, and therefore detect, 5 ppm of ethanol. However, some materials stood out: P25DMA doped with TiO_2 , NiO, and Al_2O_3 , along with PPy, had the best sensitivity towards ethanol. In terms of selectivity, P25DMA doped with 5% Al_2O_3 and P25DMA doped with 10% TiO_2 had the best selectivity towards ethanol with respect to five typical interferent gases (acetaldehyde, acetone, benzene, formaldehyde, and methanol).^[56]

Some of the most promising polymeric sensing materials were then deposited onto two different kinds of sensors: a capacitive radio frequency identification (RFID) sensor and a mass-based microcantilever microelectromechanical systems (MEMS) sensor. These sensors were evaluated for sensitivity, selectivity, and response and recovery times. It was found that P25DMA doped with 20% NiO had a detection limit of 3 ppm on the RFID sensor,^[64] while P25DMA had a detection limit of 5 ppm on the MEMS sensor.^[65] Additional ethanol sensors using designed sensing materials (including siloxane-based materials and polymer arrays (containing P25DMA)) have since been investigated.^[66-68]

Working in a targeted, sequential manner made it possible to hone in on promising polymeric sensing materials for ethanol detection. We can take into consideration the chemical nature of the target analyte (and thus, the dominant mechanisms by which it is likely to interact), any constraints of the target application (including operational temperature and type of sensor), and the chemical nature of common interferents present with the target analyte. These prescriptions allow one to narrow down a starting list of hundreds or thousands of potential sensing materials to a manageable few, which can then be evaluated. Of course, this process still takes time; careful selection and

analysis is required. However, when the final product is selected, it can be used with more confidence.

4.1.3 Polymeric Sensing Materials for Acetone Detection

A third volatile organic compound for detection in small quantities (for several reasons) is gaseous acetone. Breath acetone concentration is correlated with blood glucose levels, which is especially important for people living with diabetes. If this relationship can be exploited, the physiological change could be detected through a simple and non-invasive breath test.

Designing sensing materials for acetone was largely informed by prior work. Not only had a database of potential polymeric sensing materials (and relevant properties) been developed,^[50] but practical prescriptions for the selection of such sensing materials (as shown in Figure 5) had already been established.

Given the objectives and constraints for the application, material properties (solubility parameters, desirable functional groups, glass transition temperature, etc.) were used to screen a database of 50 potential polymeric sensing materials (compiled by Stewart^[50]). Preliminary screening led to a list of five potential sensing materials (based on comparable solubility parameters and appropriate glass transition temperatures). Finally, based on previous studies, three polymer backbones (polyaniline (PANI), polypyrrole (PPy), and poly(methyl methacrylate) (PMMA)) were considered ‘most promising’ and were selected for experimental evaluation trials. At this stage, customization potential was also considered, and three metal oxide dopants (SnO₂, WO₃ and ZnO) were investigated.

The preliminary experimental work in this case involved the synthesis and evaluation of 30 candidate polymers (three polymer backbones with varying levels of three metal oxide dopants).^[69] Since it was still part of the preliminary investigation, the experimental procedure was relatively uncomplicated^[57]; sensitivity and selectivity measurements provided a good overview of the materials’ performance. The results from this stage (along with additional background information

from the literature) made it possible to identify the most promising materials and to discern the most important variables, which ultimately led to the synthesis of more customized materials.

Ultimately, data from the preliminary experiments indicated that the polymer backbone was much more influential than the type or quantity of metal oxide dopants. Therefore, new customization techniques (without metal oxide addition) were considered for the two most promising backbones: PANI and PPy. In this case, two new modification techniques (oxalic acid-doping and copolymerization) were also investigated, but any number of new formulations could have been investigated at this stage. Of course, the final stage involved re-evaluating the new materials, with additional characterization as needed. In theory, one could continue to iterate the design/synthesis/characterization process as many times as needed to achieve the desirable properties.

This particular study highlights the importance of the iterative nature of the design framework. The original design of experiments included three carefully selected polymer backbones, based on the screening steps described earlier. After synthesis, the preliminary characterization experiments indicated that PANI and PPy both had promising sorption potential, but PMMA performed poorly. In spite of the fact that PMMA had been widely advertised elsewhere as a viable sensing material for acetone detection, the sorption observed in this preliminary experimental work was negligible.^[69] This was true for all PMMA-based materials in the study, with and without metal oxide dopants. Thus, the preliminary design stage was revisited. Since the functionality of PMMA was still of interest, alternate approaches were considered. For example, higher molecular weights of PMMA were tested. New metal oxide incorporation techniques were attempted. PMMA synthesized in-house was compared to PMMA purchased directly from suppliers. In all cases, regardless of the approach, the acetone sorption of PMMA was negligible. Ultimately, the decision was made to accept this ‘negative’ result and to focus instead on the other backbones, namely PANI and PPy.

Generally speaking, these types of ‘negative’ results are deemed unworthy of publication; the carefully selected polymer backbone did not behave as expected, and so it can be tempting to keep the result quiet. However, ignoring the result altogether seems wasteful, as the insights obtained

from this ‘negative’ result could prevent other researchers from pursuing a similar investigation. Also, for the acetone sensing application, PMMA may still be useful as a ‘zero-sorption material’, which can establish a baseline in sensors or sensor arrays; this can help reduce the number of false positives in a given sensing study.

In any case, the iterative nature of the design approach is an extremely useful aspect. When the application target is not met during the first attempt, this should not be considered a failed attempt (it is not from an information gathering standpoint). New insights can be acquired, and these will inform subsequent steps. Ultimately, this sequential and iterative approach will lead towards optimality.

4.1.4 Polymeric Sensing Materials for Detection of Surrogate Gases

Given the experience with designing polymer sensing materials for the applications cited above, one could design detector materials for another application in a much shorter period of time (for instance, our group was recently asked to design and test materials (over a 6-month period) for the detection of formaldehyde and benzene). Chemical similarities between chemical warfare agents and simple aldehydes can be exploited for preliminary testing of sensing materials. Specifically, if the goal is to detect phosgene (a chemical warfare agent), a surrogate gas like formaldehyde can be used; they are chemically similar (they contain a carbonyl group and are similar in size), yet formaldehyde is significantly less toxic. For the preliminary evaluation of materials, formaldehyde was selected as the main surrogate gas, but acetaldehyde (which is slightly larger, as a molecule) could also be used for evaluation.

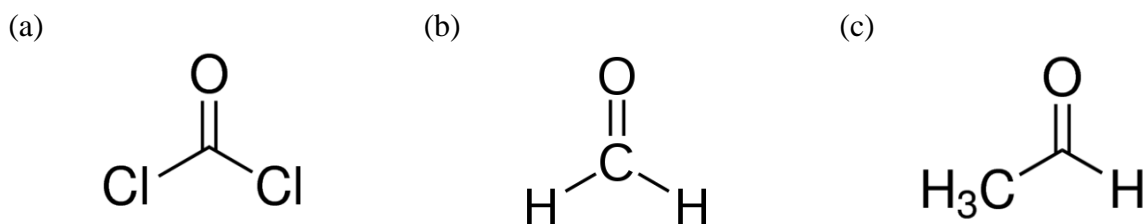


Figure 7: Similarity of chemical structures of (a) phosgene, (b) formaldehyde and (c) acetaldehyde

Benzene was selected as the interferent gas for this study, as it is representative of aromatic hydrocarbons. It is the least complex aromatic hydrocarbon and is a good representative of interferent (rather large) gases for the application.

As described previously, the goal in designing sensing materials is to promote interactions between the gas analytes and the polymeric materials through various sensing mechanisms. In this case, there is potential to take advantage of the carbonyl group, since it is common to phosgene and (less toxic) aldehydes. Three properties that can be employed are polarity, hydrogen bonding, and Lewis acid-base behaviour.

The characteristics of aldehydes (and, by extension, warfare agents like phosgene) described by Stewart and Penlidis^[58] were considered in the selection of sensing materials. Initially, four polymeric materials were selected and analyzed: polyaniline (PANI), poly(2,5-dimethyl aniline) (P25DMA), poly(4-vinylpyridine) (P4VP) and poly(acrylic acid) (PAAc). Through a series of experimental trials, the sensitivity of the selected materials (that is, the affinity of each material toward the target analyte) and the selectivity of the selected materials at various concentrations (with benzene as the interferent gas) were evaluated. Experimental results indicated that most promising materials for the application were PANI and P25DMA.

In collaboration with the 'sensor group' (led by Professor E. Abdel-Rahman, Systems Design Engineering, University of Waterloo), small quantities of these materials were deposited onto functional sensors. To achieve this, 1 g polymer (PANI or P25DMA) was mixed with 50 g of ethylene glycol (ethylene glycol facilitates polymer dispersion for pumping and subsequent deposition, and is volatile enough that the solvent can evaporate naturally from the sensor's end plate). The mixture was then deposited onto the sensor using a microfluidic pump (10 $\mu\text{m}^3/\text{min}$) through a pipe-pipette assembly to deposit a 10 μm^3 droplet onto the end plate. The solvent was then allowed to evaporate naturally, leaving the detector polymer on the plate (see Figure 8 and Figure 9).^[70]

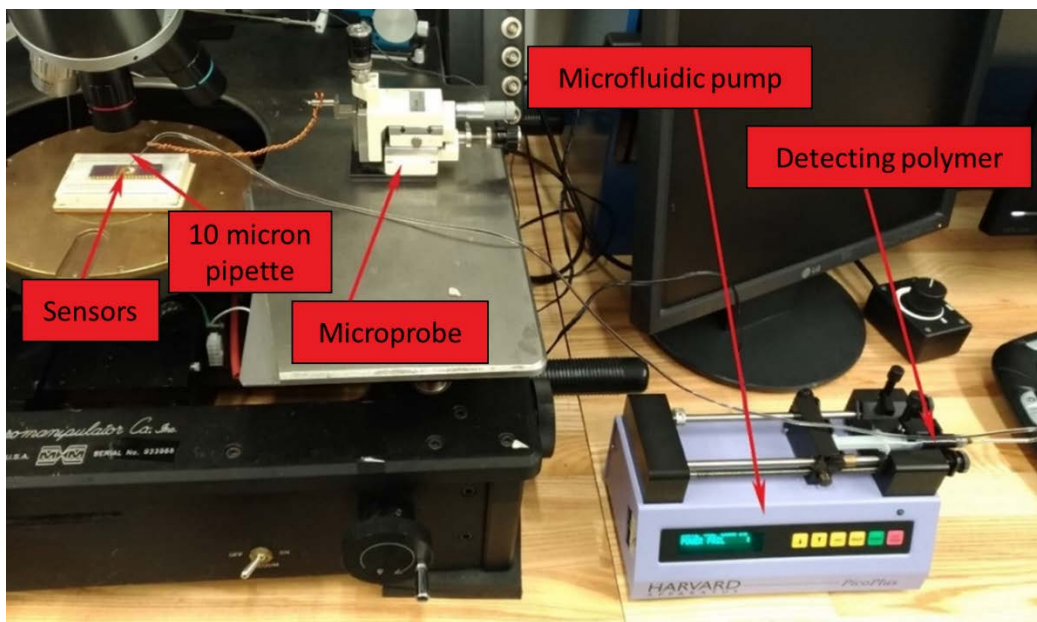


Figure 8: Deposition of polymeric material onto sensor plate

Figure 9a shows the sensor before the deposition process, while Figure 9b shows the successful deposition of P25DMA onto the sensor; this deposition process was developed by PhD student M. Arabi (Systems Design Engineering), in collaboration with and with support from our group.^[70]

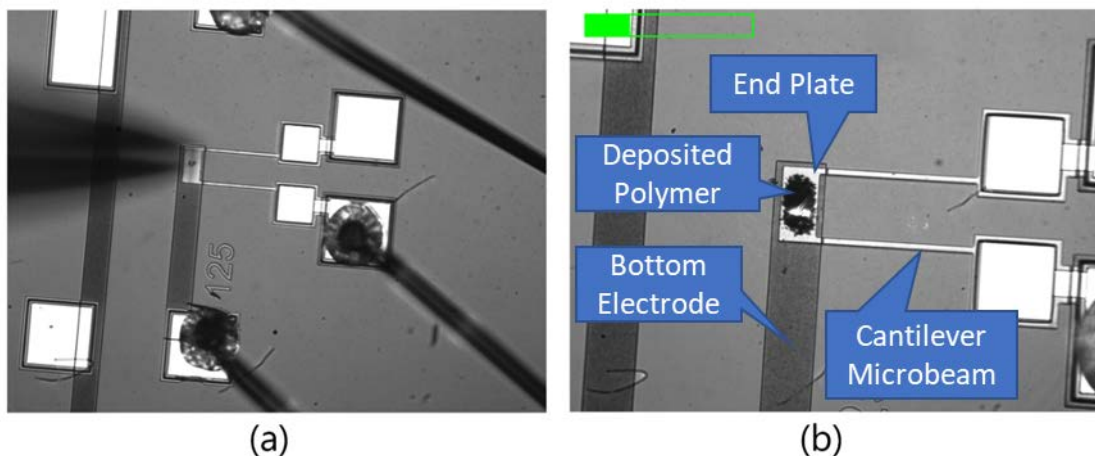


Figure 9: Sensor (a) before and (b) after polymer deposition

Again, the main focus of this work is the design of sensing materials, but one can apply the materials to different sensors given a target application. For this particular study, our ‘polymer group’ observed good selectivity of formaldehyde in the presence of benzene (for both PANI and

P25DMA) and the ‘sensor group’ was able to develop new microscale and very sensitive gas sensors for the detection of formaldehyde. The collaborative angles and the shortening of the overall investigation period are evident, as mentioned in the examples of Section 2 as well.

4.1.5 Takeaway Points for the Design of Polymeric Sensing Materials

Instead of blindly starting with a material, characterizing it and then evaluating it as a sensing material, these results should convince researchers to use a more targeted approach. Sensing materials can be designed by determining the predominant mechanisms by which the target analyte is likely to interact with the sensing material. This can significantly reduce the number of sensing materials that actually need to be evaluated. Essentially, the database of candidate sensing materials (‘long-list’) becomes a ‘short-list’ when chemical interactions are carefully considered, and that ‘short-list’ becomes shorter still when preliminary evaluation of sensing properties is performed experimentally. Thus, only a small handful of materials (in which we are much more confident) need to be deposited onto sensors for further evaluation (a much more expensive step). This systematic approach considerably reduces the material requirements and the experimental investment needed to find (and eventually optimize) appropriate sensing materials for a targeted application.

An interesting extension of polymeric sensing materials is their use in sensor arrays. Sensor arrays or electronic noses (e-noses) combine multiple sensing materials into one sensor, and the response from each of the sensing materials is incorporated into some algorithm (often an artificial neural network or a model coming from multivariate statistics), which analyzes all of the data and provides an output where specific analytes are identified. The algorithms are used, in principle, to discriminate between different analytes through pattern recognition. Fine-tuning an algorithm can improve the selectivity of a sensor array for a specific application. However, as a proof of concept, widely available cluster analysis tools such as principal component analysis (PCA) can be used.^[71,72]

Finally, it is important to note that the design of polymeric sensing materials is not limited to gaseous analytes; polymeric sensing materials can also be designed for the detection of toxic

aqueous analytes. This can be significantly more challenging than gaseous analytes, since the water effects must also be considered. As an example, work by Al-Ghamdi et al.^[73] has led to the development of a polymeric sensing material (polyacrylamide) and the design of a functional electrostatic microelectromechanical systems (MEMS) sensor to identify mercury acetate in water. Thus, (collaborative) opportunities for the design of polymeric sensing materials continue to emerge; the potential applications are innumerable.

4.2 Case Study 2: Water-Soluble Polymers for Enhanced Oil Recovery

For the enhanced oil recovery investigation, the challenge is to design a water-soluble polymer that performs better than the materials that are currently used for polymer flooding. Polymer flooding, which is a form of chemical enhanced oil recovery, relies on injecting a dilute (aqueous) polymer solution into an oil reservoir. The depleted reservoir may have a significant volume of oil remaining, even after primary recovery (driven by natural reservoir energy and artificial lift processes) and secondary recovery (gas injection, waterflooding, etc.) steps; flooding with a polymer solution allows for third-stage recovery of much of the residual oil. Adding small quantities of polymeric material to the flood water impacts effective permeability through the reservoir and increases the viscosity of the displacing fluid, which improves mobility control (i.e. the mobility of the displacing fluid relative to that of the displaced oil) and ultimately enhances the efficiency of the oil recovery process.

In general, the most widely used synthetic polymers for EOR are polyacrylamide-based materials (such as hydrolyzed polyacrylamide, HPAM). Polyacrylamide-based materials are relatively inexpensive, easily obtained, and perform fairly well in EOR applications. Specifically, HPAM is widely used in polymer flooding because it provides good control over viscosity and effective permeability. However, there is room for improvement when the mechanical and thermal stability properties of HPAM are considered. It would be extremely beneficial (in terms of application performance) to minimize shear degradation of the polymer backbone, especially at the high temperature and high salinity characteristic of oil reservoirs.

4.2.1 Design of Copolymers for Enhanced Oil Recovery

This case study is based on the PhD thesis by Riahinezhad.^[74] The objective of the work was to create tailor-made copolymers of acrylamide (AAm) and acrylic acid (AAc) with specific desirable properties for enhanced oil recovery (EOR) polymer flooding applications.

In light of the design framework described in Section 3, much of the first stage ('awareness of existing materials and methods' as per Section 3.2) occurs behind the scenes (as it often happens, since there is always some prior information available). Of course, one must have a good understanding of application requirements before undertaking such a project. In this case, we have a range of fundamental polymer properties (molecular weight averages, polymer composition, microstructure, etc.) as well as application-specific properties (viscosity modification, shear resistance, mobility control, etc.) that must be considered.^[75] In terms of selecting a polymer backbone, the study followed Ashby and Johnson's 'selection by similarity'^[47]: the investigation built on existing solutions for the application. However, the most critical (and likely the most time-consuming) aspect at this stage of the design process is the comprehension of product customization techniques. AAm/AAc copolymer application performance (that is, polymer flooding performance) is tied to copolymer properties, which in turn are related to the kinetics of the copolymerization. Therefore, to truly understand how to customize the product, the copolymerization kinetics must first be well understood.

To outline the steps required for this EOR study, Riahinezhad developed an 'experimental plan' as shown in Figure 10; the first part was to perform a systematic study of copolymerization kinetics and copolymer properties, which provided the required understanding of possible influential factors in both recipe (i.e., feed mixture formulation) and operating conditions. Then, once those relationships were known, it was possible to manipulate the influential polymerization variables in order to produce optimally designed copolymers.

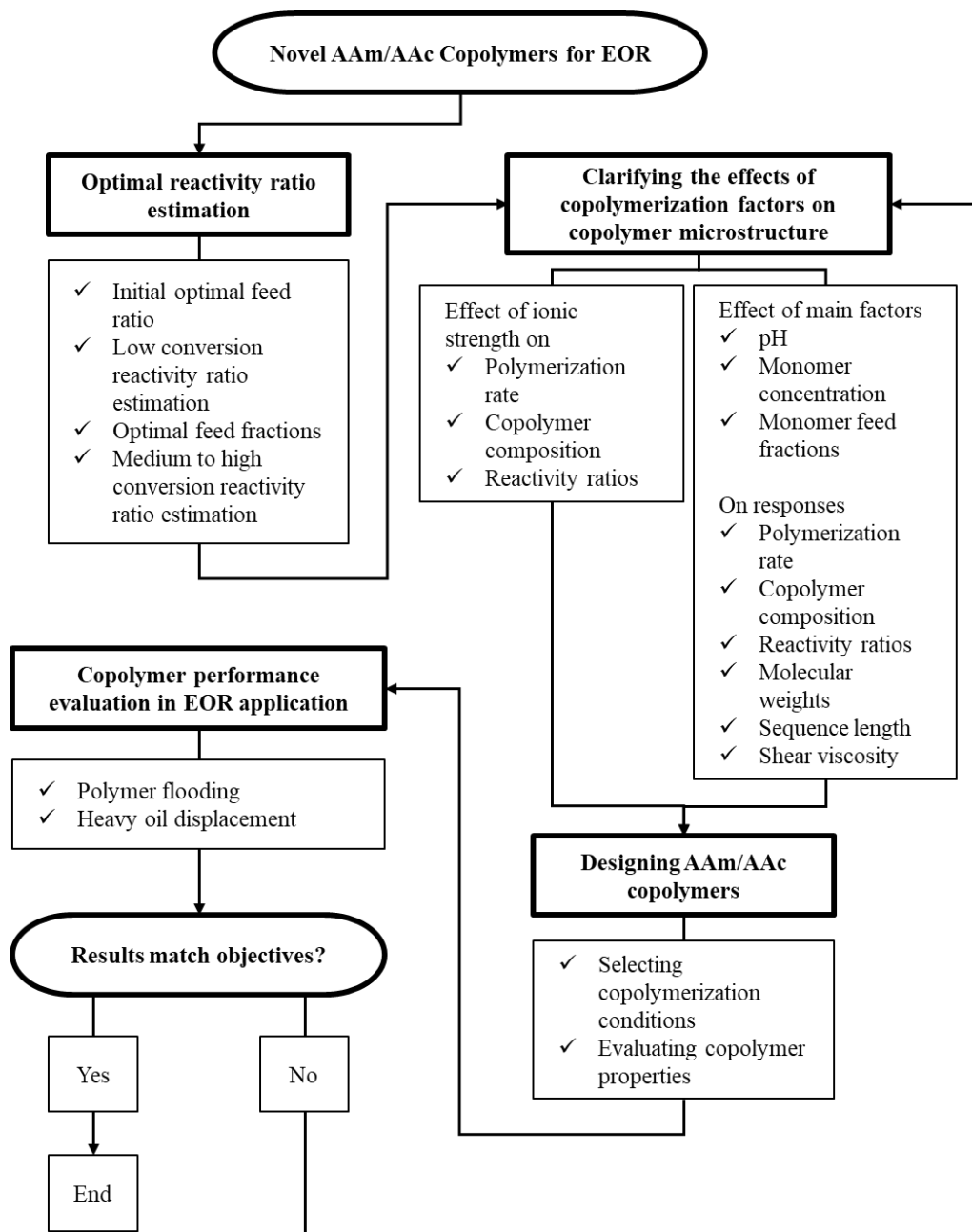


Figure 10: Overall experimental plan for related copolymerization study ^[74]

First, reactivity ratio estimates needed to be clarified. Information about the kinetics of AAm/AAc radical copolymerization were rather scarce when this investigation began, and there were significant discrepancies in the reactivity ratios reported for AAm/AAc copolymerization. Reactivity ratios, which are related to the degree of incorporation of each comonomer in the

product polymer, can be reliably estimated with the error-in-variables-model (EVM) framework along with a direct numerical integration (DNI) of the copolymer composition model.^[76] The reliability of the results was confirmed with extensive and independent replication. Furthermore, via an EVM-based criterion for the design of experiments using mechanistic models,^[77] optimal feed compositions were calculated, and optimal reactivity ratios were re-estimated for the first time based on information from the full conversion range.^[78]

With respect to copolymerization kinetics, the polymerization medium is known to play a significant role (especially in terms of pH and ionic strength), given the polyelectrolyte nature of the system. Therefore, the largely unstudied effects of solution pH, ionic strength (salt addition), monomer concentration, and monomer feed fractions ('key variables', as per the second stage of the design framework (recall Section 3.3)) were investigated in detail.^[79,80] Statistical design of experiments was used throughout this investigation, which ensured that as much information as possible could be obtained without excessive experimentation. Characterization of the polymer products indicated that feed and polymerizing mixture conditions affected monomer reactivity ratios (and, therefore, copolymer composition and microstructure), as well as other polymer properties (including molecular weight averages and shear viscosity of polymer solutions).^[81] Acquiring a better understanding of polymerization kinetic profiles and of the resulting polymer properties ultimately made it possible to manipulate influential factors for tailoring AAm/AAC copolymer properties for the desired application.^[82,83]

Once the effects of copolymerization factors on copolymer microstructure were established, Riahinezhad et al.^[82] could move toward the design of optimal materials. Again, having a good understanding of desirable application properties (including target molecular weight averages, desirable polymer microstructure, appropriate cumulative copolymer composition, optimal shear viscosity, etc.) is critical. Knowledge of desirable properties, along with an understanding of how to manipulate reaction conditions to achieve said properties, makes it possible to work towards optimality. Riahinezhad et al.^[82] synthesized four designed copolymers with carefully selected reaction conditions and acrylamide fractions ranging from 65% to 95%. All materials exhibited high molecular weights and high shear viscosity, two characteristics that are desirable for the EOR application.

Finally, the four optimally designed materials were tested in a sand-pack system: a lab-scale experimental set-up used to simulate an oil reservoir.^[83] First, displacement tests were performed to compare the flow behaviour of the newly synthesized (optimal) polymers to commercially available materials. Displacement tests involve flooding a pre-characterized sand-pack system with brine, then with polymer solution, and then with additional brine. Of the four materials, two polymers performed well, but the other two created injectivity issues and clogged the sand-pack. Therefore, only the two best-performing materials were evaluated further. The final evaluation step was oil recovery testing, in which the amount of original oil in place (OOIP) that could be recovered via polymer flooding was experimentally determined. Both of the designed copolymers evaluated at this stage had improved incremental oil recovery over the commercially available reference material. That is, in comparing ‘how much more’ oil can be recovered after polymer flooding with each material (compared to simple water flooding), the materials developed using a design approach performed better than the (commercially available) reference material.

In parallel to this EOR study, kinetic data were being collected for two related copolymers: 2-acrylamido-2-methylpropane sulfonic acid (AMPS)/acrylamide (AAm) and AMPS/acrylic acid (AAc).^[84] Careful design of experiments, data collection (especially copolymer composition), and reactivity ratio estimation for these systems (combined with the comprehensive analysis of AAm/AAc copolymerization described already) helped to build the foundational knowledge required for the following study: design of AMPS/AAm/AAc terpolymers for EOR applications.

4.2.2 Design of Terpolymers for Enhanced Oil Recovery

Extensions from the copolymer of AAm/AAc were largely motivated by the need for a more mechanically and thermally stable polymer for the EOR application. Polymer stability is an important consideration in EOR, as the polymer-containing flood water is often subjected to hostile conditions. One of the biggest mechanical concerns, especially for acrylamide-based polymers, is the shear stability of the material; the polymer is typically exposed to high flow rates (and therefore high shear stresses), which is known to cause backbone degradation. This ultimately reduces the molecular weight of the polymer, which in turn reduces the viscosity (and efficiency) of the

polymer flood water. Also, it is well-known that reservoirs at high temperatures can promote fast, severe thermal degradation of polymer molecules.^[75]

Therefore, given the background provided by Riahinezhad and coworkers,^[74,78-83] a terpolymer with improved mechanical and thermal stability was pursued.^[46] Now, a good understanding of existing materials and methods (as well as application requirements) had already been acquired, so the first decision-making point was the identification and selection of a polymer backbone. As one might expect, the AAm/AAc copolymer was a good place to start, but adding a third comonomer could improve polymer properties for the eventual application. Several comonomers were considered, but 2-acrylamido-2-methylpropane sulfonic acid (AMPS) was eventually selected. The bulky sulfonic acid group can protect the main chain (due to steric hindrance) and increase viscosity.^[85,86] In addition, strong hydrogen bonding will increase the polymer's solubility in water. Recent studies have also shown that copolymers containing AMPS are more stable in conditions of high temperature and high salinity.^[86-88]

As Riahinezhad experienced in the early stages of the AAm/AAc study, multicomponent polymerization kinetics (and especially reactivity ratio estimates) are often ignored entirely, and the values that are reported vary widely. The same is true of the AMPS/AAm/AAc terpolymer and associated copolymers; the primary focus tends to be on synthesis, characterization, and potential applications via selective testing. Since the characteristics (and application requirements) of the EOR polymer can be directly related to its microstructure, it is important to have a clear understanding of the terpolymerization kinetics. Since this information was not available in the literature, reliable reactivity ratios for this AMPS/AAm/AAc (and associated copolymer systems, AMPS/AAm and AMPS/AAc) system were determined experimentally as a preliminary aspect of this research.^[84,89]

A necessary consideration, even at this early stage, was the discrepancy between binary and ternary reactivity ratios. There is a widely-accepted analogy that binary reactivity ratios (for the related copolymers) are applicable to terpolymer systems. However, that is not always the case (especially for complex systems like AMPS/AAm/AAc), and using the binary-ternary analogy (even as an approximation) requires making considerable (sometimes unfounded) assumptions about the

system.^[90,91] Therefore, early experimental work was informed by the EVM-based criterion for designing experiments for ternary reactivity ratio estimation.^[92,93] Carefully replicated data collection and appropriate (ternary) reactivity ratio estimation led to an improved understanding of the polymerization kinetics at this stage.

Once the groundwork had been laid for the AMPS/AAm/AAC system, the investigation moved to the design of preliminary experiments.^[94] Key variables (that is, pH, ionic strength, monomer concentration, and feed composition) were identified based on related homopolymer and copolymer behaviour. While observations made for homopolymers and copolymers do not always apply to the related terpolymer, having some background knowledge can help inform decisions about experimental conditions. Therefore, a definitive screening design (design of experiments methodology) was used to establish the effects of key variables on polymer properties of interest. This experimental design allowed for the evaluation of 4 key variables (at three levels each), in just 9 experimental runs (syntheses). Two additional (complementary) synthesis runs were performed, which provided enough information for this preliminary stage.

These results were sufficient to predict how solution pH, ionic strength and monomer concentration could be used to influence the properties of the resulting terpolymer.^[94] As for the copolymer case, these relationships could then be exploited to design customized materials for enhanced oil recovery and other applications. With desirable properties in mind (and a newfound understanding of how to target them), two optimal terpolymer formulations were selected. Both terpolymers were fully characterized, from fundamental properties (molecular weight averages, cumulative terpolymer composition, microstructure, and rheological properties) to application-specific requirements (thermal stability, flow through porous media, and oil recovery performance).^[95] Both of the optimally designed materials performed better than (or as good as) currently available reference materials. In fact, in terms of overall oil recovery, the two optimally designed materials were able to recover 78.0% and 88.7% (respectively) of the OOIP, whereas the reference material recovered 59.8% of the OOIP.

Thus, the design approach was successfully employed to synthesize, characterize and test (rank) optimal materials for enhanced oil recovery. We have acquired a wealth of information about the

AMPS/AAm/AAC terpolymer, our model predictions were accurate, and our hypotheses for further performance were valid. Therefore, we can be confident in the application performance of these optimally designed terpolymers and can count on (almost) excellent oil recovery results.

4.2.3 Takeaway Points for the Design of Polymeric Materials for Enhanced Oil Recovery

Again, it is important to emphasize the sequential, iterative nature of this design process. Sand-pack tests are extremely time-consuming and require large sample quantities. Therefore, it would be impractical to experimentally evaluate the oil recovery performance of each sample produced during the preliminary experimental stage. By incrementally narrowing down the options (using improved polymerization kinetic understanding and structure-property relationships), researchers can become much more targeted in their approach, saving valuable time and resources. In this case, the improvement was quantifiable as the design approach progressed. In the first stage of the program (copolymerization), 4 optimal materials were tried, 2 worked better than the others, and testing took almost 12 months. In the second stage of the long-term program, 2 optimal materials were developed, both performed very well (better than the reference material), and testing/material evaluation took only 4 months. To put these scales in even better context, the whole investigation took almost 9 years, from posing the research objectives to testing the materials under polymer flooding conditions.

5. CONCLUSIONS

Emphasis in polymer research has shifted from synthesis to polymer reaction engineering (and scale-up) to process engineering (optimization and control) to product quality (structure-property relationships) to polymer product design. Trial-and-error approaches are not suitable for the development of materials with desirable polymer properties; not only are they inefficient, but such approaches may never lead to optimality. Therefore, to impart desirable properties to a polymer product, targeted design strategies should be employed.

Linking synthesis/polymerization/modification conditions to polymer properties (and, subsequently, to application performance) takes a substantial amount of background work; such

efforts take time. Starting with a strong knowledge of existing materials and methods ensures that application requirements are well-understood, that appropriate polymer backbones are selected, and that customization is achievable. Then, statistical design of experiments (to inform preliminary experimental work) allows for a targeted approach. One can learn a great deal about a system, while simultaneously minimizing the experimental effort required. Such preliminary (screening) investigations are an important aspect of relating system variables to resulting polymer properties. These relationships can eventually be manipulated to obtain materials with desirable (optimal) properties. Finally, theoretically optimal materials can be further characterized to ensure that all desirable properties have been obtained. Of course, the entire design process is sequential and iterative; each step builds on knowledge gained in the prior step, and some experimental stages may need to be revisited under different conditions. In any case, the framework described herein can be used as a 'road map' to assist with the design process.

The examples and two more in-depth case studies shown herein have demonstrated the versatility of the suggested design framework. This framework has been useful and relevant for design of several polymeric materials, and we hope to continue using it as we pursue additional customized polymer products. The effectiveness of using a design approach is visible throughout the research process, and it is especially evident when we see the application performance of the final product. Of course, any tools (mathematical, statistical and computational) that may speed up the overall design process and the evaluation of the optimal materials are always welcome.

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