ABSTRACT

Gas separation by membranes is a rapidly growing field. It has been recognized as one of the most recent and advanced unit operations. Most commercial gas separation membranes in use today are based on the defect-free and high performance asymmetric membranes. Since the membrane is the heart of the gas separation processes, research and development in this field has been continued extensively. This paper reviews the route that has been taken in developing defect-free and high performance asymmetric membranes for gas separation processes through the combine effects of primary phase inversion process and rheological factors. The former controls general morphology of membrane whereas the latter further affects molecular orientation in membrane. The development of these aspects represents a major breakthrough in membrane technology.

Keyword: gas separation, asymmetric membranes, molecular orientation, rheology, phase separation

INTRODUCTION

Membranes have become an established technology for gas separation processes since their first introduction for commercial application in the early 1980s. Gas mixtures separation such as the recovery of hydrogen from ammonia purge gas stream and removal of CO₂ from natural gas uses membrane separation system because it offers numerous advantages over the conventional technology. Among the advantages offer by membrane are less energy requirement, small footprint and modular and compact system design.

The scientific and commercial progress in membrane science and technology had accelerated over the last twenty years through a number of routes either the development of novel membrane materials and fabrication processes or development of robust process and system design and simulation.

The membranes were fabricated through a simple dry-wet phase inversion process. This process is widely employed in developing an integrally skinned asymmetric membrane for almost all membrane processes. An integrally-skinned asymmetric membrane consists of a very thin and dense skin layer (0.1µm to 1µm) overlaying on a thick and highly porous sub-layer (100µm to 200µm with an average void size ranging from 0.01 µm to 1 µm), where both layers are composed of the same material and formed in a single operation [1-3]. The skin represents the active layer that possesses selective properties, while the substructure provides a mechanical support for the skin, with negligible effects on separation.
In asymmetric membrane, permeability of the membrane does not depend on entire membrane thickness, instead it is inversely proportional to thickness of skin layer [2,4]. Hence, a high value of permeability can be achieved in asymmetric membrane with very thin skin layer. Generally, asymmetric membrane with effective skin thickness of approximately 1000 - 5000 angstroms (Å) is classified as ultrathin-skinned membrane; whereas hyperthin-skinned asymmetric membrane possesses a skin layer with thickness much less than that for ultrathins [5]. Both of them are specifically designed to achieve practical permeability.

However, these membranes would result in defects or pinholes on skin surface due to irregular packing of kinked polymer chains and incomplete coalescence of polymer molecules in skin layer [7,8]. Solution-diffusion mechanism of permeation through membrane materials is very slow compared to Knudsen diffusion or viscous flow that occurs through nonselective pores in membrane; thus a defective area plague on membrane surface can substantially cause a dramatic loss in selectivity and prevent the intrinsic selectivities (i.e., selectivities measured on dense homogeneous films) from being achieved in very thin membranes [6].

Consequently, for any given separation, there is usually a trade-off between permeability (skin thickness) and selectivity (skin integrity), where both parameters tend to exhibit a contradictory relation, representing a major problem in productions and applications of asymmetric membranes for gas separation process. At present, new challenges are directed towards development of defect-free and ultrathin-skinned asymmetric membranes for gas separation process, in which further insight and significant progress are being made.

Although a considerable amount of literature is available on gas separation, this paper mainly describes the route taken in developing a defect-free and high performance asymmetric membranes for gas separation processes through the manipulation of rheological factors. This presents a novel approach in membrane science and technology.

**MEMBRANE FORMATION FOR GAS SEPARATION**

Membranes are fabricated by a process known as phase inversion [7]. At present, phase inversion has been universally accepted as a standard technique for fabricating commercial membranes. Phase inversion is referred to as a process whereby a homogeneous polymer solution is transformed or inverted in a controlled condition into a gel comprising a polymer rich phase where this phase will solidify to form a solid membrane structure and a liquid polymer poor phase forming the voids. Thus, decomposition of a homogeneous polymer solution into a two-phase system is made by bringing an initially thermodynamically stable polymer solution to an unstable state. The thermodynamic state of a system consisting of multicomponents can be described in terms of Gibbs free energy of mixing. Under certain conditions of temperature, composition or pressure, a decrease occurs in the free energy of mixing of the solution and this will result in phase separation of the initially stable solution into two or more phases with different compositions. The resulting membrane structure is determined by a spatial distribution of the resulting phases at the point of solidification of the polymer rich phase. This is a very versatile technique allowing all types of membrane morphologies to be tailor-made according to the separation processes of interest [7].

The phase inversion technique can be further divided into four different techniques namely, thermal precipitation, air casting of dope solution, precipitation from the vapour phase and immersion precipitation [8]. The differences between these techniques are based on differences in the desolvation mechanisms. Among these techniques, immersion precipitation is widely used in producing commercial gas separation membranes and other membrane-based separations that are presently available. In this paper, the immersion precipitation technique is discussed in detail whereas for other techniques, readers are
It has been said that the phase inversion process generally possesses the following characteristics [10].

1. **A ternary system.** The process consists of at least one for each polymer, solvent and nonsolvent component. The solvent and nonsolvent must be miscible.

2. **Mass transfer.** This process starts at the interface of the polymer film and the coagulation medium resulting in increasing nonsolvent concentration in the film. Compositions changes are governed by diffusion. No mass transfer takes place in the case of thermally induced phase separation.

3. **Precipitation.** As a result of the increase of nonsolvent content, the polymer solution becomes thermodynamically unstable and phase separation will occur. Phase inversion is therefore related to the demixing phenomenon and phase equilibria and the kinetics of phase separation are important due to the dynamic nature of membrane formation.

In immersion precipitation, two types of phase separation or liquid-liquid demixing mechanisms have been distinguished resulting in two different types of membrane morphology [9,11].

1. Instantaneous phase separation and
2. Delayed phase separation

In instantaneous phase separation, the membrane is formed immediately after immersion in the nonsolvent bath. The resulting membrane structure typically consists of a very thin but microporous skin layer and an open-cell finger or sponge substructure, which is suitable for microfiltration and ultrafiltration applications [9]. The process that is responsible for this rapid phase separation is called spinodal decomposition. This will be addressed explicitly when discussing the types of phase inversion processes in the following sections. However, if delayed phase separation occurs, the resulting membrane structure often possesses a relatively dense, non-porous and thick skin layer, supported by a closed-cell sponge-like substructure [9].

Immersion precipitation can also be classified as a wet or a dry process, which can further affect membrane structure. The distinction refers to whether the casting knife or spinneret is exposed to air or is submerged directly in a nonsolvent coagulation bath. Another subtlety in the process of immersion precipitation is the possibility of a nucleation and growth mechanism due to binodal decomposition. This can form either a latex or a closed cell structure depending on the conditions.

If a substantial time is allowed in the dry stage for partial evaporation of solvent from the cast or spun membrane prior to immersion into the coagulation bath then the process is called dry/wet phase separation.

The dry/wet phase separation process requires more attention to dope solution formulation than the other methods. Recently, advancements in dope formulation and fabrication technique have evolved [12-15]. The following sections describe in more detail the formation of integrally skinned asymmetric membranes by different phase inversion processes for the production of gas separation membranes. The following techniques are applicable to different membrane geometries since the basic principles applied in the development of asymmetric membranes are the same for both flat sheet and hollow fibers. However, fiber spinning involves additional complexities due to simultaneous precipitation from both inner and outer coagulants.

**Wet Phase Inversion Process**

Membrane formation by a wet phase inversion process involves three main steps namely, 1) casting of dope solution 2) immediate immersion of the cast dope into a liquid nonsolvent in a coagulation bath and 3) post-
treatment of the membrane. Generally, wet techniques require the cast dope solution to be in lasting contact with the liquid nonsolvent in the coagulation bath. The solvent/nonsolvent exchange brings the solution to thermodynamic instability. The membrane structure is formed by solidification of the casting dope solution. Wet phase inversion for a typical polymer such as polysulfone can be illustrated with the aid of ternary phase diagram such as that shown in Figure 1 [16,17].

The phase diagram of the ternary mixture shows a miscibility gap over a large range of compositions. The corners of the triangle represent pure components i.e. polymer, solvent and nonsolvent and a points within the triangle represent a mixture of the three components. In this region the binodal boundary (or the locus of the precipitation points) and spinodal boundary can be observed. The division of these regions occurs at the critical point, CP. The tie lines connect points on the binodal boundary that are in equilibrium. The composition within this two-phase region splits into two equilibrium phases along the tie line and are known as the polymer rich, PR and the polymer poor, PP phases - each on opposite sides of the critical point. The phase separation process is induced at a point denoted by * anywhere within the two phase boundary. The corresponding tie line dictates the composition of the resulting two equilibrium phases and the relative proportions are given by the position of the point * on the tie line.

In the wet phase inversion process, when a nonsolvent is introduced into a homogeneous polymer solution resulting in an unstable mixture, the free enthalpy of the system is decreased when the solution splits into two phases. This split can occur by one of the following mechanisms: by the nucleation and growth of the less prevalent phase or by spinodal decomposition [18]. If the mixture composition * lies between the binodal and spinodal lines then nucleation and growth of the PP or PR phase occurs producing, initially, either a closed-cell structure or a latex respectively depending on whether the original mixture lies above or below CP [11,16]. Either of these two nucleation and growth structures is thought to be unsuitable for gas separation membranes due to low permeability and low mechanical integrity respectively. The closed-cell mechanism tends to produce a non-porous but excessively thick skin. However, the phase separation must not be allowed to linger as this would allow coalescence of the PP phase, which would cause defects. The latex mechanism, on the other hand, tends to produce a thin weak porous skin but this could in fact be densified in the subsequent processing steps.

It has also been suggested that skin formation in wet phase inversion may occur by rapid outflow of solvent through a gelation process. The high viscosity of the gel layer suppresses phase separation due to kinetic limitations on nucleation and growth. A skin layer that is both ultrathin and defect-free is very difficult to obtain for asymmetric membranes made by the wet phase inversion process. Process variables that favour the formation of an ultrathin skin layer are 1) low polymer concentration in the dope solution, 2) short evaporation period, 3) addition of nonsolvent to the dope solution and 4) rapid precipitation, that is, instantaneous phase separation in the quenched membrane. However, these process variables are

Figure 1: Schematic diagram of an isothermal ternary phase diagram showing the equilibrium tie lines connecting equilibrium compositions on the binodal curve having polymer rich and polymer poor compositions indicated as PR and PP respectively [16,17]
contrary to those that favour the formation of defect-free skin layers. Therefore, optimization of the formation variables is necessary to yield optimum membrane properties.

If the point * located within the spinodal boundary, instantaneous phase separation occurs without the need to form nuclei. This phase separation process is called spinodal decomposition. Spinodal decomposition involves propagation of critical concentration perturbations having a characteristic dimension that tends to be reproduced instantaneously throughout the entire macroscopic region undergoing the phase separation [11,16]. This process leads to the formation of very thin but microporous skin layer if the morphology can be trapped by sufficiently rapid solvent removal to vitrify the polymer rich phase. However, at low polymer concentration, nucleation and growth and spinodal decomposition tend to produce a similar membrane.

Generally, membranes formed by instantaneous phase separation exhibit a solution diffusion mechanism in gas separation, only when cast or spun from high concentration polymer solution and coated with silicone rubber to form multicomponent membranes.

In the case of delayed phase separation, the membrane solidifies after a certain time lag. Initially, only solvent is lost from the dope solution and the binodal line is approached 'gently' from the outside. This results in a single gel phase polymer solidification mechanism, which produces the nonporous skin. Ultimately, delayed phase separation, will produce a membrane with a dense nonporous but rather thick skin layer supported by a closed-cell, sponge-like substructure. This type of membrane exhibits the solution diffusion separation mechanism and is potentially useful for gas separation processes. However, the fluxes associated with such membranes are rather low as the closed-cell support tends to add resistance to gas flow.

Recently, a unique modification of the coagulation bath in wet phase inversion has resulted in a controlled delayed phase separation system for the formation of defect-free integrally skinned asymmetric gas separation membranes. This technique is called the dual-bath coagulation method [19] where membranes are formed within two nonsolvent baths in series. The first bath contains a weak nonsolvent causing delayed phase separation (gel) resulting in the formation of a nonporous skin layer. The second bath contains a strong nonsolvent that causes instantaneous phase separation (spinodal) in the remaining membrane structure. Using the modified dual bath coagulation technique, Li et al. [20] reported higher than intrinsic selectivities for polyethersulfone after solvent exchange drying. The defect-free skin layer thickness reported was around 0.3 µm. The dual bath technique is therefore highly promising in terms of industrial exploitation.

Dry/Wet Phase Inversion Process

Integrally skinned asymmetric membranes can also be fabricated by a process called dry/wet phase inversion [13,16,21,22]. In this process, phase separation in the outermost region is induced by solvent evaporation and the remaining membrane structure is subsequently formed by solvent-nonsolvent exchange during a quench step. This concept is known as forced convective evaporation-induced phase separation. The physical events occurring during the evaporation step have been acknowledged as the most important aspect of dry/wet phase inversion for the production of asymmetric membranes for gas separation [17].

Recently, Pinnau and Koros [12,22] produced an ultrathin defect-free skin layer by using a dry/wet phase inversion process. The skin layer achieved was of the order of 200 Å. They also developed some empirical rules for the formation of optimised membranes using this technique [17].

1. The casting solution must consist of at least three components: the polymer, a solvent and a nonsolvent. The solvent must have a higher vapour pressure than the nonsolvent component, so that phase separation can be induced during an evaporation step.
2. The composition of the dope solution should be as close as possible to the thermodynamic instability limit (binodal composition).

3. The evaporation should be carried out by forcing a gas stream across the cast membrane to induce phase separation in the outermost region of the cast film (dry phase inversion).

4. The quench step (wet phase inversion) should be carried out in a thermodynamically strong nonsolvent for the membrane forming polymer. The quench medium must be miscible with the solvent and nonsolvent of the dope solution.

The evaporation process for a typical ternary dope solution used for the preparation of membranes made by dry/wet phase inversion is schematically represented in Figure 2 [16,20]. Point A represents the initially stable dope solution. It is located near the binodal boundary. During the evaporation induced phase separation step, a gas stream is blow over a cast or spun dope to encourage solvent outflow and thus bring a few microns of the nascent membrane into a spinodally decomposed structure with an average composition denoted as \( \text{A}' \). This instantaneous process can be witnessed by the onset of turbidity in the surface of the nascent membrane [16]. If the spinodal structure in the outermost membrane region vitrifies instantaneously during the subsequent quench step (wet phase inversion) without the material having undergone further structural changes during the initial evaporation process, it is expected that the skin layer of the quenched membrane would be microporous.

In the development of this theory, Pinnau and Koros [14] reconciled the physical events occurring during the drying of a latex to produce a nonporous film with the events in the evaporation step that produce a nonporous membrane skin. They proposed that capillary pressures resulting from the gas-liquid interface in the polymer poor region cause the nodular regions of the polymer rich phase to coalesce. The coalescence is faster in membrane production than in latex drying because of the presence of considerable amounts of plasticising solvent and nonsolvent components in the polymer rich phase, which reduce the rigidity modulus of the nodule.

The condition for nonporous skin formation requires that the force resulting from capillary pressure exceed the resistance of the polymer nodule to deformation. For the spinodal network, the two interpenetrating continuous media are composed of the polymer-lean phase pervading the void space between the polymers rich-phase. Only the outermost region of the

Figure 2: Schematic representation of diffusion paths initiating near the binodal boundary and potentially penetrating to the metastable (nucleation and growth) region (A'), the unstable (spinodal decomposition) region (A") or the solidus tie line" (A"') where the morphology is vitrified immediately upon phase separation and unable to evolve [16,17]
membrane is exposed to the high capillary pressures arising from the curvature of the gas-liquid interface between nodules of the polymer-rich phase. The capillary forces tend to deform the nodules of the solvent-swollen polymer-rich phase, promoting elimination of interstitial surface voids of the polymer poor phase. Thus a defect-free gel-like surface layer is generated, as schematically depicted in Figure 3.

The capillary pressure, $P_c$, can be estimated by the Young-Laplace equation for perfect wetting conditions (contact angle equal to zero) [16,17]:

$$P_c = 2\gamma/r$$  \hspace{1cm} (1)

where $\gamma$ is the surface tension of the interstitial fluid and $r$ is the effective radius of the throat that exists in the plane passing through the centres of the three touching spherical nodules. Compressive stresses are estimated to be greater than 100 atm during the evaporation step thus causing the coalescence of the nodules. The conditions required for nodule coalescence can be related to the shear modulus, $G$, of the polymer rich nodule. The following expression was suggested:

$$G < 35\gamma/R$$  \hspace{1cm} (2)

where $R$ is the nodule radius.

If the composition of the polymer rich nodules exceeds the solidus tie line during the evaporation step then the glassy nodules will fail to coalesce due to their high rigidity (high $G$) and a microporous skin layer will be obtained. Excessively high polymer concentrations in the casting/spinning dope should therefore be avoided.

The dry evaporation step described above results in a compact, but minimally coalesced homogeneous skin resting on top of a secondary layer of uncoagulated dope. The subsequent quench step instantaneously transforms the highly plasticised, but homogeneous skin layer into essentially a solvent-free glass containing only an equilibrium amount of the quench medium. As the quench medium diffuses across the homogeneous skin layer, solvent and nonsolvent contained in the underlying secondary layer are able to move by counter-diffusion into the miscible quench bath thus causing the wet phase inversion of the secondary layer/substructure. Vitrification of the secondary layer should occur as rapidly as possible, to avoid any loss of the interconnectivity and porosity. The use of thermodynamically strong nonsolvents such as water and methanol in the quench bath allows the bicontinuous secondary layer to solidify almost instantaneously [12,22] thus causing an open-cell, sponge-like substructure [9,16].

One of the major problems confronting the use of membrane based gas separation processes in a wide range of applications is the lack of membranes with high flux and high selectivity. During fabrication, membrane formation process plays an important role and certain factors need proper attention in order to produce a good gas separation membrane. Currently, gas separation membranes technologies are challenged to maintain their favorable economics while improving their gas selectivity, flux and...
durability. The improved membranes would be attractive in large potential markets such as CO₂/CH₄, hydrocarbon/H₂ and olefin/paraffin separations [23,24]. Though extensive research and development are being devoted to develop high performance membrane, most of the works done were still based on manipulation of the phase inversion factors. Phase inversion factors control general morphology of membrane and hence determine basic capability of membrane for gas separation. Phase inversion factors, including forced-convective evaporation time, polymer concentration and solvent ratio, have been identified as dominating fabrication factors in controlling skin thickness and skin integrity, and thus have substantial effects on separation properties of resultant membranes. However, this section explores potential route in improving the separation characteristics of membranes through rheological approach, which has demonstrated significant improvement in the separation performance.

Using this technique, essentially defect-free skin layers membranes has been produced. Even without surface coating, the selectivities obtained were similar to those in dense nonporous polysulfone films. This technique has been successfully employed for a variety of glassy polymers either in flat sheets [14,21,22] or in hollow fiber geometries [15]. The wet and dry/wet phase inversion processes are the most widely used for membrane fabrication. In the present discussion, dry/wet phase inversion process is employed for the fabrication of defect-free and high performance hollow fiber membranes.

**IMPROVING THE SEPARATION CHARACTERISTICS THROUGH RHEOLOGICAL APPROACH**

**Rheological Factors**

Formation of asymmetric membranes through manipulation of rheological factors is a novel approach in membrane technology, which provides a potential platform to develop defect-free and ultrathin-skinned asymmetric membranes for gas separation. Rheological factors would affect morphology, physical properties and separation performance of asymmetric membrane. Recently, rheological factors in membrane formation processes have been extensively investigated by Ismail, Shilton and Chung [25-33].

Membrane formation process involves casting of a homogeneous multicomponent solution. Behavior of solution behavior under shear is described by response to tangential stress, which is related to molecular orientation or preferential alignment of randomly coiled chain molecules [25]. If the relationship is linear then the fluid is said to be Newtonian;

\[ \tau = \eta \dot{\gamma} \]  

where \( \tau \) is the shear stress, \( \eta \) is the viscosity and \( \dot{\gamma} \) is the shear rate. If the relationship is non-linear, the fluid is said to be non-Newtonian;

\[ \tau = k \dot{\gamma}^n \]  

where \( k \) and \( n \) are constants for the particular fluid. \( k \) is a measure of the consistency of the fluid, a high value of \( k \) indicates a more viscous fluid. \( n \) is a measure of the degree of non-Newtonian behaviour; if \( n > 1 \) the fluid is said to be shear thickening whereas if \( n < 1 \) the fluid is shear thinning. This empirical relationship is known as the power law proposed by de Waele and Ostward [25]. Polymer solution is often shear-thinning suggesting a progressive alignment of polymer molecules under shear in flow direction [25,26]. Rheological tests were carried out using a rheometer, and a typical behavior of a shear thinning solution is shown in Figure 4 [25]. The dashed line represents

![Figure 4: Shear stress versus shear rate curve for shear thinning fluid](Image)
Newtonian behavior and the solid line represents non-Newtonian behavior (shear-thinning) under shear. Stretching of polymer chains between entanglement junctions leads to a decrease in solution viscosity [25].

A substance is viscoelastic if it exhibits both energy dissipation and energy storage in its mechanical behavior. A viscoelastic fluid will exhibit a Trouton ratio (the ratio of shear viscosity to elongational viscosity) of greater than 3 [25]. A higher value of Trouton ratio indicates greater viscoelasticity. Viscoelasticity relates to the relaxation time of the solution, which is the characteristic time of the exponential stress decay curve. The relaxation time can be determined by conducting a creep test whereby a viscoelastic fluid will respond in the manner depicted in Figure 5 [25].

After an instantaneously imposed stress, the strain of the sample is monitored over time. The stress is then released and the relaxation, reflected in negative strain or recoil, is observed as a function of time. After any instantaneous yield, the non-linear region of the curve, C₁, relates to strain growth, which is controlled by combined viscous and elastic effects. This region is called the retardation period. After all elastic yield is exhausted pure viscous flow prevails. This is reflected in the linear (constant shear rate) region depicted by curve C₂, which corresponds to a steady shear viscosity. When the stress is released, point C₃, elastic recovery will occur. Combined viscous and elastic effects again control the rate of recovery. This is the relaxation period and corresponds to curve C₃ to C₄. In this period the fluid recoils due to polymer chain relaxation and eventually reaches equilibrium. The strain is not recovered completely because of the viscous flow in region C₂. Relaxation relates to a number of separate strain increments each decaying exponentially with time. Each increment is governed by elastic and viscous influences working together analogous to a spring and dashpot system. The total relaxation time of the fluid is the summation of the characteristic decay times of each strain increment. Analysis of the relaxation region of the creep curve, C₃ to C₄, allows the relaxation time to be calculated.

The relaxation time is significant in membrane fabrication. As phase separation progresses, the relaxation time will actually increase due to the onset of solidification. As long as phase separation occurs quickly, then the material has no chance of relaxing and hence the orientation will be frozen into the membrane. In fact, relaxation times become progressively longer at lower levels of residual strain and thus some level of orientation would still be likely even if phase inversion is delayed. The relaxation time indicates the level of viscoelasticity in polymer solutions and hence the level of molecular orientation induced under shear.

During casting a shear thinning and viscoelastic solution, polymer molecules are maintained in an oriented (partially) conformation by castline deformation. After casting, polymer molecules would relax to some preferred state. However, they recover only a portion of their total deformation [34]. The as-cast membrane is then going through forced-convective evaporation. Dry phase separation progresses instantaneously and limits conformational and configurational rearrangement especially in nascent skin region. Polymeric material has no chance of relaxing and therefore shear-induced molecular orientation will be frozen into nascent skin layer of membrane [17,25,26,35]. Besides that, dope formulation is tailored to be close to thermodynamic instability limit and approaching cloud point curve. Nonsolvent is added into polymer solution in order to speed up preprecipitation of phase-separated structures and reduce relaxation effects on molecular
orientation [31]. In addition, shear fields (over a certain value) can distort phase diagram and hence alter phase stability, demixing and precipitation kinetics of membrane formation process [32]. The nascent membrane is then immersed in a coagulation bath for wet phase separation. The nascent skin layer with sufficiently rigid structures is solidified immediately to form a well-defined skin layer with enhanced molecular orientation [27].

By phase inversion, Serkov and Khanchih [36] examined the development of molecular orientation during the precipitation process of polymer solution. They found that preorientation was developed during precipitation, which significantly determined the subsequent stretchability, structure and physical properties of the spun fibers. Molecular orientation by ionotropic coagulation is only applied to polyelectrolyte precipitation. Due to this limitation, the mechanism cannot be adopted to explain the structural alignment in polymeric solutions generally. Serkov and Khanchih suggested that as the front moves through the solidifying medium, orientation is developed. They also postulated that as the polymer rich phase solidifies, spherulites could form if the energy of interaction with the solvent is high. This process can lead to highly ordered structure at the molecular level. Referring to shear flow, Takuechi et al. [37], studied the morphological development in a copolyester fiber with increasing shear rate. They observed a skin-core structure in the resultant extrudate and characterized this in terms of band pattern, which were monitored through a polarizing microscope. Bousmina and Muller [38] also proposed a mechanism responsible for the development of ordered structure in an extruded filament according the influence of shear. They described a process which particles become aligned in the shear direction as shown in Figure 5. Figure 5 illustrated the mechanism considering the non-Newtonian velocity profile across the extrudate and described a process by which particles become aligned in the shear direction. Serkov and Khanchih [36] also postulated that shear-induced orientation was frozen into the skin of a fiber during formation, while the molecular orientation was induced by elongation flow. Perepelkin [39] outlined the principle aspects in the structural reorganization of polymer solutions that are; 1) a change in the orientational and three dimensional order of the structure, 2) an increase in the degree of orientation of the crystalline and amorphous sections of the structure, 3) a change in the conformational arrangement of the molecule chain and 4) a change in the molecular structure.

In gas separation membrane, it has been acknowledged that molecular orientation in the active layer will affect the selectivity. In recent years, besides the phase inversion process being the primary factor to determine the separation performance of gas separation membrane, more researches have been focusing on the rheological aspect. For that reason, rheological conditions during manufacturing will affect membrane performance by altering molecular orientation. The shear during casting and spinning is one of the important rheological factors. It was shown that molecular orientation was intensified with the shear rate increment during casting and spinning and that there is a favorable effect on selectivity. The shear rate for flat sheet membrane varies with drag time. On
the other hand, the hollow fiber membrane varies with dope extrusion rate.

Shilton et al. [29] found that permeability and selectivity rose with increasing dope extrusion rate for coated fibers due to the combined effect of enhanced polymer selectivity and increased in surface porosity. However, elongation experienced during spinning was found to be detrimental to membrane performance. Permeability increased but selectivity decreased with increasing jet stretch ratio or elongation. This was due to increase in porosity in the skin layer and unfavorable polymer structure. To explain their findings, Shilton et al. [29] suggested that shear and elongation affected the selectivity of the solid polymer in the membrane by altering molecular orientation. The actual rise in selectivity of the coated membranes with increasing dope extrusion rate could be explained by observing the increase in the selectivity of the polymer itself. This was related to the rheological behavior of the spinning dope under shear.

Aptel et al. [40] spun polysulfone ultrafiltration hollow fibers and found that the performance of the membrane depended on the extrusion rates of the polymer solution and on the bore liquid. According to them, shear forces in the spinneret caused orientation of polymer molecules which in turn affecting pore shape. If gelation of the solution due to contact with the coagulant liquid is faster than the relaxation time of the polymer solution, the polymer chain alignment is frozen into the membrane wall.

Ismail et al. [41] indicated that increasing molecular orientation occurred in the high-shear membranes. The gas permeation results are shown in Table 1. Furthermore, the selectivity of these membranes was heightened and even surpassed the recognized intrinsic selectivity of the membrane polymer. The results suggested that increased shear during spinning would increase molecular orientation and, in turn, enhanced selectivity. The selectivities were much greater for high shear membrane [35,41].

<table>
<thead>
<tr>
<th>Dope Extrusion Rate (cm³/min)</th>
<th>( \frac{P_{CO_2}}{CO_2 aCH_4} ) (cm³ (STP)s⁻¹ cm⁻²cmHg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>13.7, 37.5</td>
</tr>
<tr>
<td>2.5</td>
<td>38.5, 83.1</td>
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Takuechi et al. [37] studied the morphological development in a copolyester fiber with increasing shear rate. They observed a skin-core structure in the resultant extrudate and characterized this in term of band pattern. Takuechi et al. [38] also studied the texture of the extrudate by birefringence and showed that with shear rate induced, molecular orientation was concentrated only in the skin layer. Both Takuechi et al. [37] and Bousmina and Muller [38] suggested that, understanding and quantifying, whenever possible, the relationship between extrudate morphology and rheology was the outmost importance in optimizing processing conditions.

Spectroscopy has become an important tool to investigate the morphological characteristics of a membrane at the molecular level. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been used to characterize the surface structure, in particular the molecular orientation, in wide variety of polymer films, fibers and glass fibers. In polymer films, DRIFTS was capable of providing good quality spectra and structural information of polymer surfaces up to nanolevel thickness [42]. Reflection infrared spectroscopy has the advantage of being able to analyze the surface layers of opaque films or fibers. Recently, the technique has been developed to determine orientation of polymer molecules in asymmetric hollow fiber and flat sheet membranes for gas separation. By using FTIR, plane polarized infrared absorbed more strongly when the plane polarization is parallel. There is a difference in absorption between parallel polarized and perpendicularly polarized radiation and this phenomenon is known as linear dichroism [28].
Khulbe et al. [43] employed electron spin resonance and Raman spectroscopy techniques to study the different morphologies in integral-asymmetric and symmetric membranes of poly(phenylene oxide) (PPO) and polyamide (PA). They found that molecular orientation existed in the skin layer of the asymmetric membranes and this was responsible for greater selectivities. This orientation was subsequently related to molecular vibration in specific bonds in the membranes. Pronounced infrared dichroism (the difference in absorption between parallel and perpendicularly polarized light) indicates that the alignment of molecules, with the absence of dichroism showed that a sample had been randomly orienting the molecules. Polarized IR spectra of hollow fiber membranes had been recorded by IR reflection from samples of the fibers wound several time round a KBr plate of rectangular cross section. In this study the membrane were cast at low and high shear rate. Both membranes exhibit dichroism in the infrared, but the effect is more pronounced in the high shear membranes suggesting greater molecular orientation [35].

Molecular orientation in the active layer of these membranes was directly and quantitatively measured using plane-polarized reflectance infrared spectroscopy as shown in Figure 6. This technique could reveal anisotropy on the molecular level within a sample by pronounced infrared [35,41,44].

Shear and elongation during spinning have been proven to affect the permeation performance of polysulfone hollow fiber membranes [28,40] and this was attributed to molecular orientation in the active layer. If special skin formation conditions prevail, increased shear can create an oriented and highly ordered membrane active layer which can exhibit selectivities significantly greater than the recognized intrinsic value for the isotropic polymer. In addition, the membranes have been tested recently using positron annihilation lifetime spectroscopy (PALS) to further investigate the conformation of the active layer at the molecular level [35].

Wang et al. [45] and Chung et al. [46] suggested that hollow fiber membranes spun with high shear rates apparently have a thicker dense skin layer, indicating increasing gas transport resistance because of shear-induced chain orientation and packing. This result might also imply that a high shear rate may yield a hollow fiber with a “denser” selective layer with a lower permeability. At low shear rates, the permeances of non-polar molecules such as H₂, O₂, N₂, and CH₄ decreases, while their relative selectivities increase with an increase in shear rates. Once a certain shear rate is reached, all permeances increase, while their selectivities decrease with an increase in shear rates. In low shear rate regions, the decrease in permeance or increase in selectivity with increasing shear rates arises from the better molecular orientation and chain packing induced by shear. With increasing shear in high shear rate regions, the increase in permeance or decrease in selectivity is mainly attributed to relatively porous skin structures induced by the low viscosity nature of a power-law spinning fluid at high shear rates, fracture, and modified thermodynamics and kinetics of phase inversion process. This work suggested that there might exist an optimum shear rate to yield optimal membrane morphology for gas separation. An increase in CO₂ permeance with increasing shear rates are possibly due to enhanced coupling effect between CO₂ and the highly oriented and closely packed fluoropolyimide molecular chains induced by shear.

Ismail et al. [47] clearly illustrated the effects of shear rate and forced convection residence time on asymmetric polysulfone membrane structure and gas separation performance. The rheologically induced
molecular orientation in membranes during casting was measured directly using plane polarized reflectance infrared spectroscopy technique. Figure 7 shows the normalized different spectrum obtained from the high shear membrane (367 s⁻¹). Pronounced positive and highest dichroism (absorption parallel to the shear direction > absorption perpendicular) were exhibited in their samples. This indicates that the polymer molecular chain was aligning in the shear direction. The highly sheared asymmetric membranes tend to exhibit greater molecular orientation in the skin layer; thus, a high pressure-normalized flux and selectivity were obtained. The mean pressure-normalized fluxes of O₂ and CO₂ were about 5.05 and 11.41 GPU, respectively. The selectivity of O₂/N₂ and CO₂/CH₄ were approximately 6.72 and 32.63, respectively, at shear rate of 367 s⁻¹.

The best membrane performance obtained based on the trade-off between pressure-normalized flux and selectivity was observed at forced convection residence time of 20s and at 367 s⁻¹ shear rate.

In addition, Ismail et al. [48,49] found that the combination of an optimizing dope formulation and casting condition produced defect-free, highly selective and ultrathin skin membranes without any post-treatment. The dry/wet phase inversion process with forced convection has provided a method of preparing defect-free and ultrathin interally-skinned asymmetric membranes. The skin layer thicknesses produced were less than 0.5 µm. Both permeability and selectivity of membrane were found to increase with high-sheared casting, which were reflected in a reduction of skin thickness as well as enhancement of molecular orientation in skin layer. These suggest that the rheologically induced molecular orientation plays a significant role to heighten membrane separation performances. As a conclusion, correlation of rheological aspects with primary phase inversion conditions had successfully developed defect-free and ultrathin-skinned asymmetric membranes for gas separation.

At present, rheologically induced molecular orientation has received considerable attention from a number of investigators since it has been recognized as the factor that significantly enhances membrane separation characteristics. Therefore, systematic study on these factors with regard to gas separation membranes is widely carried out. Further studies on the fundamental aspects of rheologically induced molecular orientation using others spectroscopy techniques are foreseen to generate a complimentary results which can be used to enrich the understanding of the molecular orientation phenomenon. Modelling of the gas transport phenomena in oriented skin membranes and determination of the interaction between the permeance and the membrane materials will be considered as one of the future research directions in membrane science and technology in view of producing a practical and high performance membrane for gas separation.

CONCLUSIONS

Increasing number of research in the formation of gas separation membrane indicates that membranes technology is fast growing area and becoming another alternative for industrial gas separation processes. The fabrication of asymmetric polymer consisting a defect-free and ultrathin-skinned layer has become the strong subject of research interest because it stresses on the importance of having high permeability and selectivity gas separation membranes. Development of defect-
free and high performance asymmetric membranes for gas separation processes with practically acceptable separation properties often exhibit defect-free skins and negligible substructure resistance. Though a lot of efforts are being devoted to membrane formation for gas separation in a number of promising areas, more research and development are still needed. Rheologically induced molecular orientation is found to be one of the most important factors if membrane performance is to be heightened beyond the generally recognized intrinsic selectivity. The aspect will be further developed since it has now confirmed that formation of super selective synthetic polymeric membranes are only possible with the combine effect of phase inversion and rheological factors during manufacturing process. Systematic and brilliant strategies are still needed in order to exploit the full potential of this technology especially in producing high performance membrane for gas separation in the next decade.

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FORMULATION ENGINEERING AND
THE PRODUCT-PROCESS INTERFACE

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INTRODUCTION

All of the products which sustain us in our daily lives – foods, pharmaceuticals, cosmetics, detergents, fibres for clothes and furnishings, paints and coatings, building materials, electronic components – are structured at a range of scales. At the smallest level are molecular structures, and it is largely the job of the chemist to devise the appropriate molecule to fulfil the need. However, selecting the molecule is not enough. At the next upper level, these molecules must be incorporated into larger structures – with other components - which will deliver them in the right way to the target environment in which they have to function. This is the area of product formulation. In most of the examples above, it is the nano- and micro-structure which controls the physical and chemical properties which are essential to the product function. For example, the structure of a food controls its texture and the way in which taste chemicals are released and perceived; the structure of a pharmaceutical may control how a powder dissolves or how an active chemical is released in the body. To produce these materials efficiently requires combined understanding of their chemistry, processing and materials science - this is a very interdisciplinary subject.

Industries making use of Formulation Engineering include some of the largest and most profitable in the world. A good example is Unilever, which has annual sales of £30 billion, and spends £0.5 billion per year on R & D, primarily aimed at formulating and re-formulating products in order to maintain a competitive edge. Its various businesses, which are summarised in Table 1, employ approximately one third of a million people worldwide.

Table 1: Unilever main business areas

<table>
<thead>
<tr>
<th>Unilever Main Business Areas</th>
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<tbody>
<tr>
<td>Product examples</td>
</tr>
<tr>
<td>Foods</td>
</tr>
<tr>
<td>Ice cream, margarine, spreads, tea</td>
</tr>
<tr>
<td>Detergents</td>
</tr>
<tr>
<td>Wash powders, soap bars</td>
</tr>
<tr>
<td>Personal Products</td>
</tr>
<tr>
<td>Creams and lotions, toothpaste</td>
</tr>
</tbody>
</table>

In each of these product areas, development is a multidisciplinary activity involving fundamental science, process engineering and “a good portion of inventiveness”. Product formulation is an area which has received little attention from university-based researchers in the past.

HOW IS FORMULATION ENGINEERING DIFFERENT FROM “TRADITIONAL” CHEMICAL ENGINEERING?

All branches of Engineering must reflect the changes in the industries they serve, or else, will become obsolete. The last three decades have seen unprecedented and irreversible changes in the

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Formulation Engineering differs from traditional process engineering in that it is much more strongly consumer-led. The products of Formulation Engineering are specified in terms of a set of consumer desirables or effects, rather than simple chemical formulae, for example. Since Formulation Engineering is driven by customer demand, which can change rapidly, processes must be designed to be flexible, enabling rapid introduction of new products. This is one of many differences from traditional process engineering. Others include the fact that processes are often operated on a much smaller scale, making high-value specialities rather than high-volume commodities and with competition on the basis of quality and innovation rather than price. A single batch of pharmaceutical active ingredient can be worth some millions of dollars.

Of course these changes are seen differently in different parts of the world, but it is already apparent that South East Asia will be able to follow a twin-track strategy of developing “traditional” petrochemicals and “new” speciality businesses simultaneously.

These global-scale industrial developments have led to more specific changes in the way chemical and process engineering is practised, particularly an emphasis on development of products at the expense of processes. Some changes in the nature of the products of the chemical and process industries are summarised in Table 3.

Figure 1 gives some examples of the industries which make use of formulation or “product engineering” according to an early pioneer in this field, Hans Wesselingh [1]. The examples of industries here are arranged according to the scale of operation. From the top downwards, process engineering becomes more important, as does the contribution of equipment to the overall operational costs. The “science” component of the operation increases in the opposite direction, while formulation or product engineering is important over the entire range. Clearly there is room for argument about the precise shape of the diagram!

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**Table 2:** Global changes in the chemical and process industries

- “Maturity” in the petrochemical industries – petrochemical plants can now be designed reliably by computational methods and operated with minimal workforces
- Progressive migration of the petrochemical industry from North America and Europe to the Middle and Far East
- The rapid development of speciality chemical businesses serving the emerging high value industries in electronics, pharmaceuticals, biotechnology, etc.

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**Table 3:** Changes in the products of the chemical and process industries 1970-2000 (after Oliver, 2003)

1970
- homogeneous commodity
- cost competition
- macro/meso scale
- (large-scale continuous process)

2000
- composite, structured speciality
- quality competition
- micro/nano scale
- (smaller scale, flexible process)
Finally, it is now an imperative for product producers to understand the life-cycle of their products and hence their overall effect on the environment. Consumer resistance to products which are perceived to be environmentally damaging is a major factor in marketing and Formulation Engineers have a major role to play in “green product” design. A recent example of reformulation, in response to these pressures, is the production of effective aerosol products without the use of environmentally-unsatisfactory compressed gases.

**PRODUCT TYPES**

The range of products of possible interest to the Formulation Engineer is vast. Table 4 gives some ideas of a possible classification.

Some consideration of the relationship between products and processes is necessary here. Clearly they are always inextricably linked, and this is even more the case for speciality products than for commodities. To take two contrasting examples, a commodity such as ethanol has no “memory” of its processing steps, but a speciality such as yoghurt certainly has [2]! The simple act of pumping can degrade its microstructure and destroy its value. Development of “formulated products” therefore, requires detailed understanding of the product-process relationships.

A further interesting difference between this work and “traditional” chemical and process engineering is that formulated products are often deliberately designed to break down in use. For example, the structure of a tablet is designed to dissolve; the structure of a paint is designed to maintain its anti-drip properties but to allow shear and spreading into a thin smooth film. The study of the processes by which the product breaks down in use is very much part of Formulation Engineering.

The remainder of this section covers some brief examples of product formulation in the three major areas identified above.

**FOOD**

Foods are structured materials: structure may be in the solid phase (for example crystals in chocolate and ice-cream; cells in meat and plant tissue) or in liquids (network or particulate gels, based on starches or milk proteins, in sauces; emulsions in spreads and creams).
Many of the processes of the industry have been developed empirically; new techniques of manufacture must generate products which have the same quality as the old. Some novel techniques and products are available, such as the production of low-fat alternatives to ‘classical’ foods which have the same attractiveness. The challenge to the processor is the efficient production of foods which are safe and attractive to the consumer.

- the structure and formation of food granules. There is as yet no reliable way of ensuring that food granules can be constructed to ensure that they (i) are strong enough to be conveyed through the food chain, (ii) are structured so that they hydrate or dissolve rapidly, (iii) have the required chemical structure and properties - for example, the surface composition often has no relationship with the bulk composition because drying of the granules has brought surface active species to the edge [3].

- diffusion and reaction in food solids: foods are complex structures through which diffusion is highly complex and non-Fickian. Diffusion controls many food properties: for example, moisture content is important, as is the motion of flavours and nutrients. It is necessary to understand the relationship between the structure of the material and the transport properties of the system: for example in plant and animal tissue to identify drying rates and associated quality loss [4].

- structuring of liquids and soft solids: structured fluids are common in food processing. Examples include (i) in oil/aqueous dispersions (such as spreads and ice-creams), where the kinetics of fluid processes, such as drop breakage and coalescence, are a function of interfacial conditions, and are in practice set by additives such as monoglycerides and emulsifiers [5]; (ii) aqueous/ aqueous dispersions (such as low fat spread formulations); (iii) soft solids (such as gels and chocolates), where shear affects the final product structure and properties.

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<table>
<thead>
<tr>
<th>Skills Areas</th>
<th>Foods</th>
<th>Pharmacy-ceuticals &amp; bioproducst</th>
<th>Personal and home care</th>
<th>Coatings and fibres</th>
<th>Agro-chemicals</th>
<th>Energy products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structured liquids</td>
<td>Emulsions/ dispersions</td>
<td>Emulsions/ creams/ dispersions</td>
<td>Creams and foams</td>
<td>Paints and film coatings</td>
<td>Dispersions</td>
<td>Fuels &amp; lubricating oils</td>
</tr>
<tr>
<td>Soft solids</td>
<td>Crystals + spreads</td>
<td>Solid/liquid dispersions</td>
<td>Crystals, creams and foams</td>
<td>Pigments + paints</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Particulate processes</td>
<td>Granules + extrudates</td>
<td>Granules + encapsulation + supercritical route powders</td>
<td>Granules + powders</td>
<td>Pigments + paints + fibres</td>
<td>Granules + extrudates</td>
<td>Fuel cell structures, catalysts</td>
</tr>
<tr>
<td>Biodelivery</td>
<td>Structures to promote flavour and nutrition</td>
<td>Structures for controlled drug release</td>
<td>Products with biological action</td>
<td>Sutures and medical fibres</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4: Skills areas, industry sectors and products in Formulation Engineering
BIOPRODUCT PROCESSING

The effective delivery of such bioproducts as enzymes, probiotics, gene therapy vectors and particulate vaccines depends on maintenance of the product characteristics during their manufacture, packaging, storage and end-exploitation. Such characteristics may be easily degraded as a result of a complex array of degradative side-reactions or system antagonisms [6]. Degradation processes may be reduced or suppressed, and end use enhanced (site targeting, biological efficacy, operational longevity, etc.) by giving attention to the details of product formulation. Product formulation (defined here as those processes which advance the efficacy, longevity and targeting of bioproducts) must be studied in tandem with the processes of manufacture, selective isolation and polishing which define the end specification of products [7].

An area of current interest is the formulation of probiotic assemblies. The assembly of probiotics involves the encapsulation or entrapment of the preserved micro-organism(s) into a particle, which permits the ready oral delivery, targeting and controlled release of the agent(s). For example, the targets for Aspergillus oryzae (which enhances cellulose digestion in humans and animals) are the small and large intestines, so that resistance to passage through the acidic stomach is essential. Processes of encapsulation based upon aqueous-based polymerisation reactions must therefore, be augmented with enteric coating procedures which impart resistance to acidic attack in the stomach and a sensitivity to alkaline solubility and controlled-release in the intestine. Studies must include not only the impact of encapsulation on the original cell viability, but also its reproducibility in scaled-up manufacturing operations.

SPECIALITY PRODUCTS

In common with food and bioproducts, the functionality of speciality products is usually derived from their complex structure, which is produced by dispersion of one phase in another – pigment in paint, for example – and the creation, maintenance and (in some cases) controlled break-down of the structure is the key to product form. For example, paints and coatings must incorporate dispersed particulate matter of precisely controlled particle size and shape, and in the required concentration, to produce the desired optical properties and resistance to degradation in use.

The dispersed structures of speciality products may have continuous gas, solid or liquid structures, such as:

• multi-phase dispersions produced by mechanical and mechano-chemical methods (for diameters of the dispersed phase entity above and below 5µm respectively)
• pastes
• agglomerated particles (for the formulation of which see [7])
• foams and other porous structures

Most pharmaceuticals and many other products such as agrochemicals require gradual or localised delivery of active species, so that structures for controlled release are required.

Current particle-formation processes rely heavily on spray drying, binder agglomeration and conventional crystallisation. During the next decades, conventional methods will give way to a new generation of techniques relying on more imaginative manipulation of the phase diagram and non-equilibrium thermodynamics. Examples include:

• supercritical fluid processing for fast reactions, giving high purity products
• cryoprocessing, incorporating ultrafast solidification/sublimation to produce very open, active structures
• sonic, electrical and microwave techniques for supplying energy in a controlled way to promote reaction, phase transformation and other structure-modifying changes.
Development of effective structured materials requires novel characterisation methods. Since most of the systems of interest are opaque, tomographic techniques are particularly useful. For equilibrium structures, x-ray microtomography provides the possibility to interrogate structures with a resolution better than $5\mu m$. By applying suitable thresholds on the basis of x-ray opacity, different features of the structure may be separated. For dynamic systems, including flow imaging within metal-walled vessels, Positron Emission Particle Tracking (PEPT) can be used [8].

**CONCLUDING REMARKS:**

**TEACHING FORMULATION ENGINEERING**

The changes in Chemical Engineering described above have stimulated new methods of teaching a product-based subject [9]; [10]. “Traditional” Chemical Engineering was about processes, often petrochemical processes, and the culmination of the undergraduate course was and remains the “Design Project” in which students design a real process from the ground up, using all their accumulated knowledge to do so. Chemical Product Engineering draws on the same basic scientific framework, but it emphasises the importance of the product. The emphasis in teaching therefore, changes to attempting to achieve an understanding of how the process variables influence the final product properties.

At the University of Birmingham, for example, students undertake a combined product and process design project. The pilot project concerns the manufacture of detergent granules and has been developed in conjunction with Unilever Research [11]. In the first week, the team members are given some Unilever product granules and are sent to purchase some rival products! They are then encouraged to think about which features of these products are most desirable and undesirable and how these might be measured in a scientific way. This is achieved by analysing the interaction of the product with the customer and its environment during its useful life and breaking this into stages which can be analysed from a Chemical Engineering perspective using fundamental principles (Figure 3).

![Diagram](image-url)

**Figure 3:** Product properties at various stages of the detergent powder life cycle
Starting from a basic formulation, and using the information they have gleaned from patents and published data, the team members are then set to produce a detergent granule for themselves, modifying the formulation and process conditions to produce the desirable features they have identified earlier. Finally, they compare the desirable features of their own product with those of Unilever’s own and the competitor products.

Following the practical project, the students design a process for producing 100,000 tonnes per annum of formulated granulated detergent powders. The brief varies from year to year and various routes may be chosen. The students must consider the problems likely to be encountered with scaling-up the process they are using, such as heat transfer and rates of reaction. Through the interaction with Unilever’s research laboratory, they have access to or are able to measure themselves the key data necessary for the design of their process.

The design project is designed to allow the student to apply the engineering skills and principles learnt during the course. The analysis of a product function requires fundamental chemical engineering to be applied in a very different but equally valid and rigorous way, using some imagination and a full understanding of the ideas behind the theories.

So far, the students who have undertaken this integrated project seem to have relished the experience. It introduces them for the first time to the Chemical Engineer’s role in product development, a role which is becoming increasingly important in most high-tech industries. Further projects along these lines are planned, in conjunction with companies in the food industry, pharmaceutical industry and speciality chemical processing.

REFERENCES


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(MEng, MA (Cambridge), PhD (Surrey), CEng, FIChemE) is Head of Chemical Engineering at the University of Birmingham and Director of Research for the new School of Engineering. He is also the first Head of the new Centre for Formulation Engineering, which was established in August 2001, with a £3 million grant from the Universities’ Joint Infrastructure Fund. Before moving to Birmingham, he was the staff of the University of Surrey (1981-94) and at Courtaulds Ltd (1979-81); he was a Visiting Professor at the University of British Columbia (1989-90) and the Technical University of Denmark (Copenhagen) (1997-2000). Professor Seville has over 100 publications, including 3 books, the most recent of which is J PK Seville, U Tüzün and R Clift, “Processing of Particulate Solids”; Chapman and Hall, London (1997).
ADVANCEMENTS IN TENSION LEG PLATFORM TECHNOLOGY

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ABSTRACT

Nearly twenty years have passed since the first Tension Leg Platform (TLP) was installed in the North Sea in approximately 150 m of water. By contrast, the eighteenth TLP will be installed in the Gulf of Mexico mid 2004 in nearly 1500 m of water. This ten-fold increase in water depth has proven that the TLP concept has evolved at an incredible rate.

The TLP has proven itself to be the system of choice for deepwater oil and gas developments. This is demonstrated by its current worldwide application in the North Sea, Gulf of Mexico, West Africa and SE Asia. The later is proven to be an ideal as well as exciting opportunity for the application of TLP technology. Ongoing developments in SE Asia are well suited to this Operator-friendly system. Also, due to the compact nature of its hull form, fabrication and integration of the system can be performed locally. The TLP can become a conduit that ties Malaysia to the global deepwater market. In addition, there are some local applications of the technology that could further develop TLPs in the quest to support Operators as they go deeper.

As an introduction, this paper first addresses the basic principals of the TLP such as its superior motion characteristics and associated operational advantages, mooring system, compact hull form, and more. The paper will then present the development of the new Extended Tension Leg Platform (ETLP) technology and its application on the two most recent TLP projects including extension of water depth, high top tensioned riser counts, quayside integration, etc. Lastly and most importantly, other technology developments pertinent to specific near-term applications in SE Asia, are presented. These include local fabrication and integration, tender assisted drilling, hull structural efficiency, and others.

Keywords: Tension Leg Platform, TLP, Extended Tension Leg Platform, ETLP, Deepwater, SE Asia, Malaysia

INTRODUCTION OF TLP CONCEPT

There are large numbers of available platform options for deepwater development. These include, but are not limited to the Tension Leg Platform, Semisubmersible, Spar, Single Column Floater (SCF), etc. To the eye, these hull forms appear very differently as shown in Figure 1. However, they can all be grouped into two families – TLPs and Floaters.

System Functions

A TLP system can support any necessary functions in deepwater. However, due to both its superior motion characteristics and its associated operational advantages as compared to Floaters, the TLP is the preferred dry completions solution. In a dry completion role, the TLP can function as a full production, drilling and quarters facility (PDQ). Or it

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can be utilized as a surface wellhead platform (SWHP), i.e. drilling and quarters are supported by the TLP with remaining functions provided by an adjacent Floating Production, Storage and Offloading facility (FPSO). In its most streamlined wellhead form, drilling systems and quarters are efficiently provided from a tender assist vessel in the more benign metocean environments.

The TLP is also a viable wet tree solution utilizing subsea tiebacks. The favorable motions of a TLP result in fewer fatigue-related concerns for Steel Catenary Risers (SCRs).

**Defining Characteristics**

Contrary to Floaters (such as the Semisubmersible, SCF and Spar), the mooring system of a TLP is vertically oriented and consists of tubular steel members called tendons. The tendons are highly tensioned using excess buoyancy of the platform hull. The highly tensioned tendon system limits horizontal offsets to a very small percent of water depth. The high tendon stiffness also reduces the system’s vertical natural periods to a level well below that of the dominant wave energy. As a result, dynamic amplification of vertical motion is nearly non-existent and the platform has limited heave, roll and pitch motions. Essentially, the vertical motions correspond to the stretch in the tubular steel tendons. For even the largest Gulf of Mexico hurricane waves of 25 m, the corresponding vertical motions of the platform are limited to a few centimeters.

The TLP’s six-degree of freedom (DOF) rigid body motions are defined in Figure 2. For those degrees of freedom in the vertical plane (heave, roll and pitch), the motions are effectively eliminated by the axial stiffness of the tendon system. As such, the sensitivity of critical operational aspects including drilling and the support of Top Tensioned Risers (TTRs) to vertical
Technology Cluster: OIL AND GAS

Platform: SYSTEM OPTIMIZATION

History

Seventeen TLPs have been installed to date worldwide. The first, Conoco’s Hutton platform in the UK North Sea, was installed in 1984 in approximately 150 m of water. Today, ABB has designed a TLP for nearly 1,500 m of water for Conoco’s Magnolia project in the Gulf of Mexico. This record-breaking platform will be installed in the third quarter of 2004.

The accelerating rate of industry acceptance of the TLP is very much linked to the concept’s rapid growth in technology. For example, specific design enhancements, such as the development of the Extended Tension Leg Platform (ETLP), have allowed the concept to carry heavier payloads into deeper water. This is effectively demonstrated in Figure 4.

DESCRIPTION OF A CONVENTIONAL TLP

The design of a TLP hull form, and particularly its distinctive mooring system, is very much linked to payload and water depth. Despite its weight-sensitive nature, the TLP has proven to be the Industry’s favored deepwater hull form worldwide for dry tree applications because of its operationally-superior motion characteristics. This has been demonstrated on a global scale with TLPs now located in the North Sea, Gulf of Mexico, offshore West Africa and SE Asia.

A brief overview of TLP configuration, motion characteristics and associated operational advantages are presented below.

Typical Configuration

A typical TLP hull configuration consists of four vertical columns that can be square or cylindrical in cross section. Rectangular pontoons connect the columns below the water surface. On top of the columns, and integral to the hull, is the structural deck that supports the topsides production facilities, drilling system, production risers, living quarters, etc. If a TLP has the capabilities for vertical access to wells, i.e. drilling or well work-over, then it is deemed to be a “dry tree” unit.

motion is eliminated. The motions in the horizontal plane (surge, sway and yaw) are controlled by tendon tension.

Offset with setdown is another very interesting aspect of TLP behavior. This is illustrated in Figure 3. The TLP experiences offset when acted upon by a horizontal force. These forces arise from wind, waves, current and other sources such as SCRs and Fluid Transfer Lines (FTLs). Due to the high axial stiffness of the tendon system, offset will be accompanied by an associated increase in TLP draft. This is called setdown. If a TLP is offset to a given position and released, the horizontal tendon tension component due to offset and the increased vertical tendon tension component due to setdown act together to restore the platform to its vertical position.

From an operational perspective, a beneficial outcome of this offset-setdown behavior is a greatly reduced TTR stroke as compared to floater concepts.
Figure 5 identifies the major system components of a typical PDQ TLP.

**Motion Performance**

The key element that enables the TLP to respond favorably to waves is the separation of the six DOF natural periods from the dominant wave energy. This is shown in Figure 6 where the TLP’s six DOF natural periods are superimposed over a typical 100-year storm wave spectrum (hurricane event) in the Gulf of Mexico. Notice that the heave, roll and pitch motions (vertical plane) exhibit natural periods at 4 sec or less and the surge, sway and yaw motions (horizontal plane) have natural periods of motion greater than 100 sec. Since both of these natural period regions fall outside the range of dominant wave energy, the dynamic response of the TLP system to waves is small.

A typical set of Response Amplitude Operators (RAOs) for the six DOF motions of a TLP are shown in Figures 7a and 7b. These RAOs represent a typical TLP located in 1,800 m water depth offshore Malaysia. An RAO can be defined as the linear relationship between the motion of a TLP (in a single degree of freedom) and a unit amplitude regular wave. For the translational motions (surge, sway and heave), the units of the RAO are ft/ft, or feet of motion per unit wave amplitude. For the rotational motions (roll, pitch and yaw), the units of the RAO are deg/ft, or degrees of motion per unit wave amplitude.
In addition, typical tendon tension RAOs are shown in Figure 7c. The units of the tendon tension RAO are kips/ft, or kips of tension per unit wave amplitude. A typical offshore Malaysia 100-year event wave spectrum has been superimposed on this plot for comparison. It can be seen that this TLP system has been optimized such that the tendon tension RAO in the range of maximum wave energy is minimized. This set of RAOs represents the fundamental motion characteristics of the platform. During a typical design process, many variables such as hull dimensions, draft, tendon cross-sectional area, tendon tension, etc. will be varied in order to obtain favorable motions. This highly important work, often referred to as Global Performance analysis, is performed over a wide range of metocean conditions, operational phases, intact and damaged conditions, and both inplace and pre-service conditions. The pre-service conditions capture all of the construction and delivery phases prior to being installed. These often include deck/hull quayside integration, dry transport, wet tow, installation, etc. The final configuration and sizing of the TLP (and therefore its motion characteristics) for a particular application can only be established once all of the above conditions have been considered.

Operational Advantages

Utilization of TLP technology for a deepwater development results in operational advantages not necessarily found with other competing hull forms. Some of the more important tangible benefits are presented and discussed below:

- Support of dry trees – The superior motion characteristics of the TLP (due primarily to the tendon mooring system) enables safe and efficient support of TTRs. The platform is able to remain operational in more severe metocean conditions. Because of the offset and setdown behavior of the TLP, riser stroke is greatly reduced compared to other competing Floater concepts. SCRs (import, export, or both) are also efficiently supported by the TLP.

- Wellbay configuration – A conventional and proven wellbay is inherent to the TLP. TTRs are supported within a grid-like wellbay centered between the TLP columns. The risers are untouched until their connection at the seabed. In comparison with other TLP concepts, riser keel joints and a centerwell (with potential hydrocarbon safety hazards) are not necessary. Also, the contiguous wellbay configuration of the conventional TLP results in reduced trim ballast requirements compared to other TLP options with split wellbays.

- Drilling and workover – The TLP can support drilling either in a self-contained mode or via tender assist. The drilling tender vessel can be moored integral to the TLP. Significant loads can also be eliminated from the TLP by physically moving drilling systems and platform accommodations to the tender vessel. The size of the TLP can then be reduced. The global behavior of the integrated TLP/tender vessel system is well understood and proven.

- Functional versatility – TLPs to date have performed many different functions and combinations. These have included:
  - Self-contained production, quarters and drilling platform
  - Wellhead platform with adjacent FPSO
  - Self-contained or off-TLP production with drilling tender assist

- Small footprint – Because the tendon mooring system is vertical, the footprint on the seafloor is small. Contrary to other Floater hull forms utilizing catenary (spread moored) mooring systems, the TLP
system will not interfere with adjacent facilities such as FPSOs, production barges, drilling tender vessels, pipelines, etc.

- Installation of completed system – The compact nature of the TLP hull (i.e. small height, width and draft) permits quayside lift of the deck and the associated integration activities. Near full commissioning of the system is also performed at quayside. Installation of a fully integrated and nearfully commissioned facility results in a shorter schedule, lower cost and reduced risk compared to equivalent operations performed offshore.

**TECHNOLOGY BREAKTHROUGH – THE ETLP™ PLATFORM**

Extensive experience and lessons learned from ABB’s major involvement in TLP projects over the last 25 years have been applied to the development of the ETLP™ platform. The ETLP™ system has proven to be a significant technology breakthrough. An overview of the ETLP™ system development history and its advantages are presented below.

**Development History**

For several years, ABB has aggressively pursued a technology development effort to revolutionize the conventional TLP. A multi-million dollar investment has been made by ABB in the development of the ETLP™ concept for a variety of topsides payloads, riser counts, water depths and regions of the world. Extensive engineering, design and physical model testing has been performed.

ABB has performed a large number of paid studies and design competitions for Clients whose deepwater development options are favorable for an ETLP™ platform. The ETLP™ concept has shown to be technically sound as it is comprised of conventional and well-proven systems.

The primary difference between a conventional TLP and the new ETLP™ platform is the hull form. Previously, tendons were connected to the lowermost outboard portion of the hull on the columns. For the ETLP™ concept, the columns have been moved inboard allowing a more favorable support condition for the deck and its associated riser and drilling related loads. Pontoon extensions on the outboard edge of the column are used as tendon connection points. Figure 8 shows a plan view of the conventional TLP and ETLP™ platform to illustrate the differences between the two hull forms.

For developments where the production riser count is low, a three-column ETLP™ platform can be utilized. This smaller version of the ETLP™ platform has undergone the same extensive development work as the four-column ETLP™ concept. The 3-column ETLP™ platform is shown in Figure 9.
Advantages

The most salient features of the ETLP™ system are related to weight reduction and the efficiencies gained in project execution through quayside integration.

Compared to a conventional TLP, the hull and deck steel weight savings of an ETLP™ platform is approximately 40%. This has been demonstrated via controlled shadow studies on recent ETLP™ system designs.

A measure of the effectiveness of the ETLP™ platform to carry topsides payload can be described by a ratio called structural weight efficiency. This ratio quantifies the weight of payload that can be supported by a given weight of hull and deck platform. The structural weight efficiency for an ETLP™ platform is high compared to a conventional TLP. For future SE Asia applications, it is interesting to note that the structural weight efficiency increases dramatically as the design metocean conditions become more benign. This is discussed in more detail in a later section.

The other significant advantage of the ETLP™ platform is its ability to be installed as a completely integrated and commissioned unit. As such, the installation operation is less complex as compared to other floating hull forms and is therefore, less likely to be adversely affected by weather.

The advantages of the ETLP™ system can be summarized as follows:

• Comprised of safe, conventional and well-proven systems,
• Greater than 40% hull and deck steel weight savings when compared to the conventional TLP,
• Integration and commissioning of topsides and hull is done quayside,
• Minimal risk exposure for installation in remote regions, and
• A large crane vessel is not required for installation.

RECENT APPLICATIONS OF THE ETLP™ CONCEPT

Two of the Industry’s most recent deepwater projects have been technically challenging for different reasons. ExxonMobil’s Kizomba “A” field offshore Angola required a SWHP to support 36 TTRs, and ConocoPhillip’s Magnolia platform will be installed in nearly 1,500 m of water in the Gulf of Mexico. In both cases, the ETLP™ platform was selected. These two projects for which this breakthrough technology has been applied are presented below.

Kizomba “A” Project

The Kizomba “A” deepwater development located in 1,178 m water depth offshore Angola (block 15) has an estimated 1 billion barrel recoverable reserves. To further enhance reservoir recovery, ExxonMobil selected a dry tree development plan that called for a SWHP tied to a FPSO with product export provided by an offtake buoy. The overall development layout for Kizomba “A” is illustrated in Figure 10.

The ETLP™ system was selected for the Surface Wellhead Platform. Functions of the SWHP include drilling, well intervention, and support of the dry tree manifold. All processing and storage is provided by the adjacent FPSO. Utilities for the SWHP’s drilling operations are also provided by the FPSO.

Figure 10: Field Layout for Kizomba “A”
Development details for Kizomba “A” are as follows.

<table>
<thead>
<tr>
<th>Kizomba “A” SWHP</th>
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<tbody>
<tr>
<td>Draft</td>
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<tr>
<td>No. of TTRs</td>
</tr>
<tr>
<td>No. of Tendons</td>
</tr>
<tr>
<td>Total Payload</td>
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<tr>
<td>Displacement</td>
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<table>
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<tr>
<th>Kizomba “A” FPSO</th>
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</thead>
<tbody>
<tr>
<td>Capacity</td>
</tr>
<tr>
<td>Storage</td>
</tr>
<tr>
<td>LxBxH</td>
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</table>

Selection of the ETLP™ system for Kizomba “A” has demonstrated that:

- Benign metocean conditions allow TLPs to carry larger payloads in deeper water
- TLP can be designed to have 100% operational uptime year round
- ETLP™ platform can be installed fully integrated and commissioned
- Using a TLP, separation distance between the SWHP and FPSO is greatly reduced as compared to other Floater hull forms

**Magnolia Project**

The Magnolia deepwater development is located in the Gulf of Mexico in nearly 1,500 m water depth. ConocoPhillips selected the ETLP™ platform for this dry tree development.

The ETLP™ platform supports full production, workover rig, 4 subsea tiebacks and 2 umbilicals. Gas and oil are transported to shore via export SCRs and pipelines. The Magnolia ETLP™ platform is illustrated in Figure 11.

Development details for Magnolia are as follows.

<table>
<thead>
<tr>
<th>Magnolia Facility</th>
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<tbody>
<tr>
<td>Draft</td>
</tr>
<tr>
<td>No. of TTRs</td>
</tr>
<tr>
<td>No. of Tendons</td>
</tr>
<tr>
<td>Total Payload</td>
</tr>
<tr>
<td>Displacement</td>
</tr>
</tbody>
</table>

Selection of the ETLP™ system for Magnolia has demonstrated that a full TLP is viable in nearly 1,500 m of water in the Gulf of Mexico and the platform can be fully integrated and commissioned prior to installation.

A recent photograph showing the Magnolia ETLP™ platform deck lift and integration at quayside is provided in Figure 12.
NEAR-TERM TECHNOLOGY APPLICATIONS FOR SE ASIA

The ETLP™ platform is ideally suited for ongoing and future applications in SE Asia. This new technology is Operator-friendly and is comprised of conventional and well-proven systems. Also, because of the compact nature of the hull form, fabrication and integration of the system can be performed locally.

Local Fabrication and Integration

Details regarding fabrication of the ETLP™ hull and deck, and deck-hull integration are outlined below. Comments relating to local construction of the ETLP™ platform are found at the end of this section.

ETLP™ Hull

Fabrication of the ETLP™ hull can be tailored to suit a number of construction methods depending upon the capabilities and strengths of a given Fabricator due to its compact form. For example, ABB has demonstrated that land-based fabrication at quayside can be equally as efficient as drydock fabrication.

For either of these methods, hull fabrication is a very systematic and disciplined process, and one that is fully integrated with engineering. The fabrication sequence begins with sub-assemblies, which form blocks, which in turn form super-blocks. Super-blocks are the largest of the hull components and are lifted into the drydock or rolled into the land-based erection area. The super-blocks are pre-outfitted to the maximum extent with equipment, piping, pipe supports, penetrations, cable trays, ladders, stairs, etc. Due to parallel design-fabrication activities, pre-outfitting is often limited by engineering supply of drawings. Painting is the last activity prior to final lifting of the super-block into place within the structure.

A total of 24 super-blocks were used for the Kizomba “A” ETLP™ hull. Because of this efficient procedure, complete erection of the hull in the drydock was performed in only six weeks. A photograph of the Kizomba “A” hull in drydock (Daewoo Shipbuilding and Marine Engineering - Korea) is shown in Figure 13.

Upon leaving the drydock, the ETLP™ hull is moved to a nearby quayside location where final mechanical completion and pre-commissioning activities are performed. Systems entirely contained in the hull are fully commissioned. The hull is then readied for transport. Figure 14 shows the float-on operation of the Kizomba “A” ETLP™ hull.

If the hull is fabricated at a quayside land-based location, all final mechanical completion and pre-commissioning activities are performed prior to direct loadout onto the transportation vessel. A photograph showing land-based fabrication (Belleli - Italy) of the Auger TLP hull is shown in Figure 15.
Once inplaced on the transport vessel and secured, the ETLP™ hull is then transported to the deck-hull integration site. A photograph showing the arrival of the Magnolia ETLP™ hull at the Gulf of Mexico integration site is presented in Figure 16.

**ETLP™ Deck**

Depending upon its size and deck-hull integration method, the deck can be fabricated in a single integrated piece or in modules.

A single integrated deck will in most cases exceed a Fabricator's lifting capacity. As such, this option will involve a float-over deck-hull integration operation.

Because of its single piece construction, the deck will generally be more structurally efficient (less redundant steel) than an equivalent modular-type deck. Due to the float-over operation, a sheltered deepwater area will be required. The hull will experience a slight growth in weight due to the increased draft (hydrostatic design head) associated with this operation.

In most cases, TLP decks have been fabricated in modules. As a general rule, fewer modules will benefit subsequent module-to-module integration activities. The Kizomba “A” ETLP™ deck was fabricated in two major modules, where the Mars TLP and Ram/Powell TLP decks were fabricated in five modules. Lifting capacity was the major factor in determining the number of deck modules for these cases.

The deck’s major truss rows are fabricated first. Deck pancake sections are then placed between the rolled-up truss rows. Deck pancake sections span between the truss rows and contain deck beams, plating and all self-contained equipment.

For the Kizomba “A” ETLP™ platform, each module was fabricated under cover in a shop. The weight of each module was kept below 6,000 mt for lifting purposes. Roll-out of the North deck module is shown in Figure 17.
ETLP™ Platform Deck-Hull Integration

Upon arrival at the deck-hull integration site, the hull is brought to quayside and readied for the deck lifting program. For Kizomba “A,” the lifting sequence of the deck and other key packages are as follows:
- North module,
- South module,
- Living quarters,
- Drilling module, and
- Drill rig including skid base, drill floor and derrick.

Figure 18 shows the lifting operation for the second, or South, module.

After all of the above lifts and associated integration activities are performed, the complete topsides are fully commissioned at quayside. This is shown in Figure 19. The fully integrated and commissioned ETLP™ system can be wet-towed to site, or loaded onto a heavy-lift submersible vessel for dry transport as shown in Figure 20.

Local Construction

A significant level of local content is achievable given the compact form of the ETLP™ platform and the well-proven nature of its associated key systems.

Construction of the ETLP™ deck and hull is possible in SE Asia and would be encouraged in order to shorten the project schedule via the elimination of lengthy transports. As discussed earlier in this section, the uncomplicated design of the ETLP™ hull allows flexibility in construction methods. Since drydock and land-based construction methods are possible, fabrication yard options can be expanded. Platform appurtenances such as boat landings, riser tensioner cassette frames and wellhead access platforms can also be fabricated locally.

Tendon piles are excellent candidates for local fabrication, and with proper training, the tendon strings themselves can also be fabricated locally. Methods have also been developed by ABB to permit safe pre-installation of the tendon system without the use of a costly heavy lift vessel.
The platform-based drilling system is typically fabricated in several modules and then transported to the integration site for assembly directly on the ETLP™ platform. Drilling system modules can be fabricated locally. Prior to final sail-away of the ETLP™ system, the completed drilling system is fully commissioned.

The top-tensioned drilling and production risers would likely be fabricated elsewhere and transported to site for direct installation on the in-place ETLP™ platform. Pre-installation of all the riser tensioner cassette frames while at the deck-hull integration site permits simple installation of the risers after the ETLP™ platform has been installed.

**Drilling Optimization**

A TLP–based system permits a higher level of drilling optimization than other competing Floater concepts. For example, Tender Assisted Drilling (TAD) reduces payload requirements on the TLP by allowing storage of drilling fluids, tubulars and other equipment on the tender vessel. Accommodations can also be founded on the tender vessel. The relocation of these loads to the tender vessel results in a smaller TLP with an associated reduction in capital costs.

The superior motion characteristics of the TLP permit simple coupling with the tender vessel, thereby, enhancing personnel and equipment transfer safety. Drilling operations are also maximized due to the reduction in weather related rig downtime.

The favorable motions of the TLP also eliminate the need for motion compensation on the drill string, an active mooring system and complex telescoping joints. In benign metocean regions like SE Asia, direct connection (hang-off) of production risers is possible, thus, eliminating riser tensioning equipment.

A brief summary of the drilling related advantages from a conventional TLP or ETLP™ platform is given below:

- No requirement for an internal centerwell (moonpool) to trap hydrocarbons
- Riser top tensioning systems are less complex due to limited motions and offsets, and are installation friendly. Buoyancy cans on risers are unnecessary.
- Reduced relative motions between tree and BOP results in riser strokes in the range of 1 m as compared to 9 m for competing Floater concepts
- Riser tensioning equipment can be eliminated in benign metocean regions like SE Asia
- A TAD approach significantly reduces weight management concerns
- Utilization of guidelines allows positive control to access subsea wellheads
- Close proximity (coupled) mooring with TAD vessel

**Elimination of Heavy Lift Vessels**

Heavy lift vessels are typically utilized for specific TLP installation related tasks. These have included: offshore deck lift and integration (with associated weather and equipment related risk), installation of foundations and tendons, and platform installation.

Unfortunately, heavy lift vessels attract very high day rates. Also, since existing heavy lift vessels are located primarily in the N Sea and Gulf of Mexico, mob and de-mob costs are typically high. These construction vessels also must be contracted early often resulting in premature definition and agreement of complex installation campaigns and windows.

Alternatively, it is possible for heavy lift vessels to be eliminated altogether in SE Asia. This is summarized in the sections below.

**Deck Lift and Integration**

The conventional TLP and ETLP™ platform are integrated at quayside. The platform can be near fully commissioned prior to wet tow to site. Lengthy risk prone offshore campaigns inherent to other competing TLP concepts and some Floaters are not necessary.
Foundation and Tendon Installation

Workable and proven alternatives exist for foundation and tendon installation. For example, suction piles (providing soil conditions are appropriate) can be used instead of driven piles. Suction piles can be reliably deployed in SE Asia from a locally obtained subsea construction vessel. Entire tendon strings can be prefabricated at a local waterside location and wet towed by tugs to site. Upon arrival, each tendon is then upended and stabbed into its bottom connector located on the suction pile. The tendon will be held vertically by a Temporary Buoyancy Module (TBM). The TBMs are removed once the TLP is connected to the tendons.

Platform Installation

It has been customary for heavy lift vessels to be onsite during platform installation, i.e. ballasting the TLP down for connection to the preinstalled tendons. In these cases, the dynamically positioned heavy lift vessel performs no real activities other than to provide additional accommodations during the installation phase. Alternatively, readily available tugs can be used to hold the TLP in position over the preinstalled tendons. The time taken for ballasting process in order to engage the tendons and a reach storm-safe tension level is approximately 12 hours.

Local Solutions

An execution plan utilizing quayside deck lift, integration and commissioning of the completed TLP facility is well proven and is the preferred solution over the more expensive and higher risk offshore alternative inherent to competing TLP concepts. Eliminating the dependence on a heavy lift vessel will encourage local solutions and thereby increase local content. The resulting impact on schedule, and flexibility of the installation window, will be positive. It is estimated that the installation related costs of a TLP in SE Asia can be reduced by half simply by eliminating of the heavy lift vessel.

Structural Weight Efficiency

One important consideration with any floating deepwater development option is its structural weight efficiency. A more structurally efficient TLP system will result in an increased topsides payload capacity and/or the ability to be applied to deeper water depths. The more structurally efficient TLP hull and deck will also typically require fewer tendons due to the reduction in system dynamics. The ETLP™ platform has a much broader range of application, because of its approximately 40% steel weight savings over a conventional TLP.

Metric for Structural Weight Efficiency

Structural weight efficiency can be quantified by comparing the total topsides payload of a TLP to its total weight of hull and deck steel. This is illustrated by the following equation:

\[
\text{Structural Weight Efficiency} = \frac{\text{Total Topsides Payload}}{\text{Total Hull and Deck Weight}}
\]

The following important definitions are provided:

**Total Topsides Payload** – Weight of all deck equipment and facilities including quarters, drilling systems, etc. Also includes TTR loads, SCR loads and secondary deck steel. Topsides equipment or facilities carried in the hull, and hull ballast earmarked for future expansion are also included.

**Total Hull and Deck Weight** – Structural steel weight of hull, hull marine systems, hull appurtenances and outfitting, and trim ballast. Also includes deck primary structural steel weight.

Based on the above definitions, the structural weight efficiency of an ETLP™ platform can be expressed as a ratio between Total Topsides Payload and Total Hull and Deck Weight. This ratio quantifies the amount of Total Topsides Payload that can be carried by a unit Total Hull and Deck Weight. Resulting from a recent
ETLP™ system design study for a SE Asia application, the computed structural weight efficiency was 1.44. This conceptual-level efficiency can be compared with the following as-built platforms.

<table>
<thead>
<tr>
<th>Hull Form / Location</th>
<th>Maturity</th>
<th>Ratio</th>
</tr>
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<tbody>
<tr>
<td>TLPs in GoM</td>
<td>As-Built</td>
<td>0.6 – 0.8</td>
</tr>
<tr>
<td>ETLP™ Platform in GoM</td>
<td>As-Built</td>
<td>1.1 – 1.2</td>
</tr>
<tr>
<td>ETLP™ Platform W Africa</td>
<td>As-Built</td>
<td>1.3 – 1.4</td>
</tr>
<tr>
<td>ETLP™ Platform in SE Asia</td>
<td>Conceptual</td>
<td>1.4 – 1.5</td>
</tr>
</tbody>
</table>

The above efficiency ratios cannot be directly compared, as different locations (regions having significantly different metocean conditions) are represented. Other aspects that contribute to a non-like-for-like comparison include differences in water depth, payload and design approach. The structural weight efficiency ratio is also affected by the maturity of the design (e.g. conceptual level design vs. as-built). As such, the 1.44 ratio for the conceptual ETLP™ platform for SE Asia would be expected to increase as the design becomes more developed.

The structural weight efficiency ratio of an ETLP™ platform improves dramatically as metocean conditions become more benign. This would be the case in SE Asia. As a demonstration of the value of the ETLP™ system, notice the improvement in structural weight efficiency ratio between the conventional TLP and the ETLP™ platform, both in the Gulf of Mexico.

CONCLUSION

The development of deepwater fields in Southeast Asia is generally complex requiring the installation of several major elements for a successful development. Among these are subsea infrastructure, dry-tree unit, and if so determined, FPSO and export shuttle tankers.

This paper has demonstrated the breakthrough technology associated with the ETLP™ platform and how it can become a conduit that ties Malaysia to the global deepwater market. Many systems of the ETLP™ platform lend themselves to fabrication in a variety of countries, allowing domestic fabrication where desirable. Developed from the TLP, the ETLP™ concept has evolved into a very safe and cost effective solution. A low risk installation operation that minimizes offshore exposure time is also possible with the ETLP™ platform.

There are significant benefits to be gained from the use of the ETLP™ concept for deepwater developments in SE Asia:

- Due to the benign metocean conditions in the SE Asia region and the inherent efficiency of the concept, the ETLP™ platform can carry larger topsides payloads and extend into deeper water depths. At this time, nearly 2,000 m water depths are possible with moderate sized payloads.
- Current technology developments are ongoing to further extend water depths and payload limits.
- With surface completions, a much higher level of reservoir management and productivity is possible given the ease of intervention.
- Tender assisted drilling from a TLP is safe and provides an opportunity to reduce the size and cost of the platform.
- The ETLP™ system has very high operational uptime for drilling and related activities due to its ability to maintain a very small watch circle even for the most severe metocean conditions in SE Asia.
- Structural weight efficiency of the concept is high for SE Asia. The ETLP™ platform can carry 1.44 mt of topsides payload for each 1.0 mt of hull and deck steel.
- Since the ETLP™ system can be installed fully integrated and commissioned, significant reductions in offshore installation time and risk are possible.
- When the ETLP™ platform is used in conjunction with a FPSO, the separation distance between the two vessels can be greatly reduced compared to other Floaters such as Spar. Flow assurance issues and fluid transfer line loads acting on the ETLP™ platform are minimized. Significant cost savings are achieved with shorter fluid transfer lines.
Local content is facilitated by the ETLP™ concept. Significant parts of the facility can be fabricated in domestic SE Asia fabrication yards.

Due to the compact form of the ETLP™ platform, fabrication of the hull can be tailored to suit a number of construction methods depending upon the capabilities and strengths of a given Fabricator.

When the economic life of a development has been reached, the ETLP™ platform can more easily be decommissioned, modified and redeployed to a new field compared to other competing TLPs and Floaters.

ACKNOWLEDGEMENT

The author would like to thank all those who helped contribute to this paper and for ABB’s continued and generous support of deepwater technology development.

John W. Chianis is currently Vice President, Deepwater Technology and Engineering at ABB Floating Production Systems in Houston, Texas. He has worked in the deepwater engineering field since 1978. His specific areas of technical competence are structural design and analysis, Naval Architecture, hydrodynamics and software development. Although he has worked on numerous types of floating hull forms, his prime area of interest over the last 24 years has been on Tension Leg Platforms (TLPs).

In addition to countless TLP studies and related development efforts, he has participated in the detailed design and delivery of the following TLPs – Jolliet, Auger, Mars, Ram/Powell, Ursa, Marlin, Brutus, Kizomba “A,” Kizomba “B” and most recently, the Magnolia Extended Tension Leg Platform (ETLP) detailed design for 4,700 ft of water in the Gulf of Mexico.
MATERIALS, DESIGN, AND MANUFACTURING ISSUES ASSOCIATED WITH COMPOSITE PRODUCTS FOR THE GAS AND PETROCHEMICAL INDUSTRY

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ABSTRACT

The composite materials and petrochemical industries have been integrally linked for decades. In the case of polymer-based composites, the relationship is truly circular. Polymer composites are based on petrochemical constituents, and products made from them are used throughout the gas and petrochemical industry. The effective development of any composite product requires the fully integrated consideration of materials, design, and manufacturing issues. The proposed presentation will include an identification of the critical issues that need to be addressed, and the relevant research work involving understanding of material behavior, design issues, and intelligent manufacturing science development that is currently being pursued at Lehigh University.

Keywords: Fatigue Crack Propagation, Composite, Design, Neural Network.

1.0 INTRODUCTION

This paper addresses the material, design, and manufacturing issues relevant to composite fabrication. For this purpose, three important research areas, which are currently being pursued at Lehigh University, namely, fatigue crack propagation resistance composite materials, design issues, and intelligent manufacturing utilizing neural network methods are highlighted in this paper.

1.1 Material Behavior

The fatigue crack propagation resistance (FCP) of polymer-matrix composites is of paramount importance when such materials are used for engineering components that are subjected to cyclic loading. The FCP behavior of model epoxy-matrix composites has been studied in the past [1 - 3] and several toughening mechanisms have been proposed. Such mechanisms include matrix micro-cracking, matrix shear banding, crack path deflection, and fiber bridging.

The focus of the study presented in this paper is to examine the FCP resistance of a series of filled epoxies where the matrix-filler adhesion has either been promoted or reduced using organosilane compounds. Moreover, the FCP behavior will be examined as a function of filler type (sphere vs. fiber) and after moisture exposure.
1.2 Composite Structural Design Challenges

Composite structures are in general not too difficult to design, manufacture and analyze, except for when it comes to features such as joints, edges and local load introductions. At present, numerical tools such as Finite Elements do not have reliable predictive capabilities for these features. Composite structures should in general be designed with as few joints and irregularities as possible. However, there are often a number of such features that still need to be incorporated. The question is then how to best accommodate these, without adding too much weight and still gain the strength and stiffness advantages expected from composites. A few relatively new concepts for joining in particular steel and composites are reviewed below. The focus of the work presented was marine structures, although many of the concepts are also applicable to other areas.

The joints discussed in this paper are mainly of the type where a steel edge was molded into a composite at the time the composite was made. Vacuum infusion was employed for most specimens. The materials used were stainless steel and glass or carbon fiber reinforced polymers. The investigations performed may be classified in two general types: adhesion and geometry related, and are discussed separately in the current manuscript.

1.3 Neural Network Based Intelligent Control of Autoclave Cure Process

The autoclave cure process is used in the production of advanced polymer composites, primarily for the automotive, marine, and aerospace industries. Historically, autoclave cure has been used to produce composite parts of high quality. One major hindrance to the production of composites through autoclave cure is that the process is largely trial-and-error, leading to much waste and parts with less-than-optimum properties.

Recently, much effort has been put into controlling the autoclave process both off-line and on-line. Off-line controllers determine processing conditions prior to cure, not allowing the variation of processing parameters during cure. Consequently, unexpected occurrences, variation in prepreg properties, and imperfect controllers lead to poor quality and much waste. On-line controllers avoid these problems by maintaining product quality in real-time (adjusting processing parameters when necessary). During this study, an on-line controller was developed utilizing the predictive capabilities of a neural network: a form of artificial intelligence designed to model the human brain’s ability to learn and devise relationships.

An autoclave is, in essence, an insulated pressure vessel that allows heat, pressure, and vacuum to be applied to a laminate (Figure 1). The laminate is laid-up by hand onto a tool plate prior to cure and surrounded by a lay-up assembly composed of numerous parts including bleeder material which absorbs excess resin, and a vacuum bag which renders the system air-tight. Each layer of the laminate is a section of prepreg tape, composed of a thermosetting resin matrix (commonly epoxy) and fibrous inclusions (including glass, carbon, and aramid fibers).

The time-dependent variation of temperature, pressure, and vacuum during the autoclave process is referred to as the cure cycle. Prepreg manufacturers provide estimates of the proper cure cycle, estimates developed through experience and trial-and-error. Such manufacturer-defined cure cycles do not take part thickness and shape, unexpected occurrences during the process, or variations in prepreg properties (such as resin content, molecular properties, and slight inclusions) into account. While manufacturer-defined cure cycles are widely used during autoclave cure, an improved method of determining cure cycles is necessary to ensure high product quality.
1.3.1 Numerical Model Based Control

One recently developed method of determining cure cycles involves the use of numerical simulations. Numerical simulations are hampered by the complexity of the autoclave process. The process involves heat transfer between the lay-up assembly and the environment, between the assembly and the prepreg, and between the prepreg and the tool plate. The process also involves chemical reactions, void formation and transport, resin flow through fibrous media, fiber compaction, and much more. The modeling of such a system is clearly an overwhelming task. In all cases, simplifying assumptions must be made to reduce the complexity of the problem. Even when simplifying assumptions are included, numerical models of the autoclave process require excessive computer time. In total, excessive run time nullifies numerical model applicability to on-line control, while inaccuracies reduce the effectiveness of numerical models for off-line control.

1.3.2 Knowledge Based Control

A solution to the problems of unexpected occurrences and variation in prepreg properties is real-time control. Real-time control has been accomplished with the use of three aides: expert systems, fuzzy logic, and neural networks. Expert system and fuzzy logic (knowledge based) controllers rely on the availability of a human expert. The human expert devises rules based on available information, rules that must be sufficient to provide control during the entire process. Formulation of this complete set of rules is difficult and time-consuming.

Some success has been achieved with knowledge-based controllers. This is partially due to the fact that rules may be devised which depend only on readily measurable quantities such as air temperature, composite temperature, autoclave pressure, and laminate compaction. In addition, knowledge based controllers need not know the shape, thickness, or components of a composite to provide adequate control. Ciriscioli and Springer [4] developed one such expert system controller. The controller provides good real-time control, allowing the creation of parts with high quality when prepreg manufacturer-defined cure cycles are less adequate or not provided.

Improvements over expert system controllers are possible. Expert system controllers raise and lower processing parameters only when rules are broken. Therefore, an incomplete or errant set of rules does not allow sufficient, continual control. Further, the magnitude of change in processing parameters is often not clearly defined.

1.3.3 Neural Network Based Control

Neural networks can provide rapid on-line prediction of cure parameters, leading to the possibility of continual, well-defined, real-time control. Joseph and Hanratty [5] demonstrated the theoretical applicability of neural network based control to the autoclave process. They applied a neural network based controller to a simulation of the autoclave process. Results from this simulated control process showed that a neural network based controller could compensate in real-time for unexpected occurrences and prepreg property variation. Results also showed that composites of the same or higher quality than from conventional cycles could be consistently produced with the neural network controller, even when unexpected occurrences and prepreg property variation are not included.

Although Joseph and Hanratty’s controller demonstrates the theoretical applicability of neural network based control, improvements upon their control procedure may be made. First, the controller was developed under the assumption that the autoclave cure cycle can be divided into four phases (based on autoclave temperature): a first ramping phase, a first holding phase, a second ramping phase, a second holding phase. While this assumption is consistent with traditional cure cycles, it may not allow for optimum variation in temperature. Second, the controller optimizes two important aspects of final part quality, void size and composite thickness, but does not inherently optimize other product quality attributes such as cure extent and cycle time. Third, as
of yet, the controller has not been deployed on an actual autoclave: all results were obtained from a numerical simulation.

2.0 APPROACHES AND METHODS

2.1 FCP Study

The model epoxy system consisted of a bisphenol A based epoxy cured with piperidine. Additional bisphenol A resin was added to reduce the crosslink density and promote toughness.

Two types of fillers were used: glass spheres with a mean diameter of 42 µm and milled glass fibers with average dimensions of 1.5 mm long and 16 µm in diameter. Both types of fillers were washed with methanol. Some fillers were treated with an aminopropyl silane (APS) to increase matrix-filler adhesion while other fillers were treated with a butyl silane (nBS) to reduce adhesion.

The epoxy resin and 24 phr bisphenol-A (phr: part per hundred parts resin by weight) were mixed at 180° under vacuum and cooled to 80°. Then, 10 volume% of reinforcement was added and mixed under vacuum. Next, 5 phr of piperidine was added and mixed for about 10 minutes under vacuum. The mixture was poured into a mold that had been preheated at 160°. Curing was performed at 160° for 6 hrs. Specimens were cut from the plaques prepared by this procedure.

2.1.1 FCP Testing Procedure

Fatigue crack propagation tests were performed according to ASTM D647 [6] guidelines using compact tension specimens (specimen size was 13.75 mm and the thickness was 6 mm). The specimens were cut from plaques that were prepared as described above. Sinusoidal loading was applied to the specimens at a frequency of 10Hz with a load ratio of 0.1 (minimum load / maximum load). Crack opening displacements were measured with a clip gauge. Crack lengths were calculated automatically using the compliance of the specimen.

2.1.2 Fractography of FCP Specimens

Fracture surfaces were observed by a JEOL 6300F or Philips ESEM XL30 scanning electron microscopy (SEM) with an acceleration voltage of 5kV. The fracture surface was covered with sputtered Au-Pd before examination. For optical microscopy, specimens were mounted in a room temperature-cured epoxy and ground perpendicular to the fracture surface and along the width of the specimen using standard petrographic techniques. These thin sections were inspected using an Olympus BH2 transmission optical microscope.

2.2 Structural Composite Design

Adhesion is affected by surface preparation, such as grit blasting, solvent cleaning, priming, etc., as well as by resin additives. Several researchers have experimented with different surface preparations and additives. For a particular glass/vinyl ester system of interest for naval applications, the following preparations were used:
- basic, which consisted of grit blasting and trichloroethylene cleaning
- AF 163-2K.06 structural adhesive film from 3M
- priming system from PolyFiber consisting of C-2200 metal surface cleaner, EP-420 epoxy primer, and EP-430 catalyst - EC-3901 structural adhesive primer from 3M
- Loctite Hysol 9430 epoxy adhesive
- KZ 55 and NZ 97 zirconate coupling agents from Kenrich Petrochemicals, Inc., added to the vinyl ester resin before infusion
- HX0603-4 hydrochloric acid (HCl) etch.

The joints presently discussed were mainly of the type where a steel edge was molded into a composite at the time the composite was made. Vacuum infusion was employed for most specimens. The materials used were stainless steel and glass or carbon fiber reinforced polymers. The investigations performed may be classified in two general types: adhesion and geometry related.
3.0 RESULTS AND DISCUSSION

3.1 FCP Studies

Figures 2 and 3 contain graphs that quantify the fatigue crack propagation behavior of the neat epoxy and the two types epoxy composites before moisture exposure. In both figures, the x and y-axes denote the applied $\Delta K$ at the crack tip and the resulting crack propagation rate, respectively.

In all cases, the glass-reinforced epoxies exhibited significant improvement in fatigue crack propagation resistance than that of neat epoxy. However, the use of different surface treatments on these reinforcements did not significantly alter the fatigue crack propagation behavior under dry conditions. Residual stresses around the glass reinforcements due to the coefficient of thermal expansion mismatch between epoxy and glass provide compressive forces towards the reinforcements. Therefore, the amount of adhesion between the reinforcements and the matrix does not affect the mechanical properties under dry conditions.

Fractography studies revealed that pinning and micro-cracking occurred when the epoxy matrix is dry. More detailed discussions on this study have been submitted for publication [6, 7].

The fatigue crack propagation behavior of the neat epoxy and glass-reinforced epoxies after moisture exposure are shown in Figures 4 and 5. As is the case before moisture exposure, improved fatigue crack propagation resistance is observed for all of the composites compared to that of the neat epoxy. In contrast to the results before moisture exposure, the fatigue crack propagation behavior after moisture exposure strongly depends on the surface treatment of the reinforcements. Glass fillers treated with nBS,
which only weak van der Waals interaction between adhesion promoter and matrix resin is expected, exhibited improved fatigue crack propagation resistance especially at high $\Delta K$ levels.

Subsequent fractography studies revealed a relatively large and visually observable damage zone ahead of the crack tip when the matrix-filler adhesion was poor and the $\Delta K$ levels are high. A shift in threshold behavior at low $\Delta K$ levels suggests that fiber bridging or crack deflection mechanisms are occurring and indeed such mechanisms were observed.

### 3.2 Structural Composite Design

#### 3.2.1 Adhesion of Vinyl Ester Composite to Steel

Figure 6 shows the average transverse strength for the spectrum of composite structure under study. The strongest was to precure the film onto the stainless sheet under a vacuum bag for 5 minutes, then vacuum infuse the vinyl ester resin, and at last postcure the film (and composite) for one hour. The preferred technique was to use the PolyFiber primer, which yielded almost the same strength as the AF 163 film but with considerably less effort. All tests were performed under dry conditions. The KZ 55 and NZ 97 zirconate additives lead to reduced strengths under these conditions. However, it is expected that they would improve strength under hot-wet conditions.

Grenestedt and Cao [8] recently performed environmental tests on disc specimens consisting of a stainless steel plate with fiberglass skin infused on top and bottom. These specimens were thermally cycled in an environmental chamber, using various humidity levels. The crack driving force was due mainly to the difference in coefficients of thermal expansion of the steel and the composite. It is interesting, although discouraging, to note that there was no appreciable debonding (interfacial cracking) when the discs were cycled in dry air, but very extensive debonding when cycling in humid air. The worst condition appeared to be cycling in high humidity and in a freeze-thaw cycle. In Figure 7, the debonded areas of a specimen is shown after different numbers of cycles.

#### 3.2.2 Geometry of Simple Joints

Regarding joint shape, a number of different concepts have been investigated. For a simple tensile loaded joint, feasible designs include single lap (shear) joints, scarf joints, and step lap joints. These may be designed in different ways. A major challenge joining dissimilar materials is that elastic mismatch leads to high stress concentrations. When the two adherends have reasonably similar compliances, the scarf and step lap joints may be designed such that the effective stiffness...
is constant along the adherends as well as over the whole joint. The average axial strain would then be constant, and desirably also the local strain would be fairly uniform. For materials with vastly different stiffnesses but similar strengths, such as stainless steel and fiberglass, this approach leads to very bulky joints. For example, if the steel were 10 times stiffer than the fiberglass but had the same strength, then the fiberglass would have to be 10 times thicker than what would be required for strength. This is certainly not an optimal configuration.

Other ways to decrease the elastic mismatch include to perforate the stiffer adherend, to taper it, to make tongues and grooves, or to make the overlap area wavy. All these schemes may be gradual, such that the stiffness of the steel is progressively decreased. These concepts are dealt with individually below.

3.2.2.1 Perforated Joints

Undén and Ridder [9] introduced the graded perforation approach, and Melograna and Grenestedt [10] used this technique for the presently considered materials. Figure 8 shows two different perforation patterns, which were investigated: circular and triangular holes. The specimens were made by placing the steel adherends between glass fiber fabrics under a vacuum bag and vacuum infusing vinyl ester resin. The strongest joint configurations were those that failed by debonding at both ends of the joint more or less simultaneously, as depicted in Figure 9. This could be accomplished by increasing or decreasing the number of rows of perforations in the steel adherend. There was no major difference in joint strength between the two perforation schemes. The best perforation patterns investigated lead to joints which were 30% stronger than their non-perforated counterparts (when no primers were used).

3.2.2.2 Tapered Joints

Figure 10 shows the edge view of the two different taper joint configurations tested. Tapering the steel adherends would be expected to reduce the elastic mismatch, at the cost of increasing through-the-thickness stresses. Such joints have been investigated by many researchers, including Melograna and Grenestedt [11] who used the presently considered materials and fabrication technique (stainless steel and vacuum infused glass fiber reinforced vinyl ester). A problem with the tapered steel adherends in
conjunction with the vacuum infusion technique was that fabrication quality decreased. The taper would lead either to waviness, or regions with less compacted fibers. The latter lead to race tracking of the resin during the infusion and areas with non-proper infusion. The result of this study was that overall, the tapered specimens were neither stronger nor weaker than their plain counterparts. If the infusions could be improved, the tapered joints would probably be superior to the plain joints.

### 3.2.2.3 Tongue-and-Groove Joints

Tongue-and-groove joints are commonly used for joining wood. Dvorak [12] used this concept to join composites and steel. Melograna, Grenestedt and Maroun [13] used it to join carbon fiber composite and stainless steel. In the latter study, nine geometrically different tongue-and-groove joint types were manufactured and tested, Figure 11. The composite was a vacuum and oven cured prepreg T700 carbon fiber / epoxy. Conventional single lap joints were also manufactured using the same materials and adhesive and with a 25.4 mm overlap. The results of the tests are presented in Figure 12. The “joint efficiency”, presently defined as the strength of the joint divided by the yield strength of the steel adherend, was approximately 43% for the single lap joint and 60% for the best tongue and groove joints. The carbon fiber composite was 40% thinner than the steel, although still stronger. With similar thickness of the adherends, the joint efficiency may be expected to approach unity for the best tongue-and-groove joints.

### 3.2.2.4 Wavy Joints

Wavy single lap joints between identical carbon fiber adherends were proposed by Zeng and Sun [14], who reported a substantial increase in tensile strength. Melograna and Grenestedt [15] reproduced these joints using different materials but the same geometry. They used the same carbon fiber composite as used for their tongue-and-groove specimens (see above). The specimens of Melograna and Grenestedt, which were considerably stronger than those of Zeng and Sun, had the opposite trend: the wavy joints were substantially weaker than their plain counterparts.

Grenestedt and Melograna [16] performed a classic Finite Element based shape optimization of a wavy joint between stainless steel and a carbon fiber composite. Such joints were manufactured and tested and proved to be approximately 15% stronger than single lap joints between the same materials.

### 3.2.2.4 Topside Joints

Various schemes for joining a composite topside structure to a steel hull have been proposed. A concept of primary interest is to attach a steel edge to the composite topside, and then weld the whole topside to the steel deck using this edge. Such concepts have been studied extensively by Hildebrand and Hentinen [17], Bohlmann and Fogarty [18] who designed and tested a bonded-bolted joint, and Clifford et al. [19] who fabricated and tested a vacuum infused joint. The latter joint was recently re-designed, manufactured...
and tested by Cao and Grenestedt [8]. The re-designed joint was both stronger and lighter. The general shape of this joint is seen in Figure 13.

3.3 Neural Network Based Intelligent Control of Autoclave Cure Process

During the present study, two real-time, intelligent controllers were developed to guide the autoclave cure process at discrete time intervals. The controllers were designed to optimize many aspects of final part quality: 1) minimum void size, 2) complete compaction, 3) minimum cure cycle time, 4) complete cure, and 5) consistent molecular properties (avoiding degradation and thermal runaway). Additionally, fewer assumptions about the autoclave process were made than with previous controllers, allowing more free control of processing parameters.

The present controllers make use of the rapid predicting capabilities of backpropagation neural networks. Neural networks for each controller were trained with data generated by a numerical model developed by Telikicherla, et. al. [20, 21]. This model incorporates many aspects of autoclave cure, including heat transfer within the autoclave environment, giving a good estimate of the total cure process. Unfortunately, the CPU time (on a Cray YMP) necessary to predict the outcome of one cure cycle is approximately 8 hours [21]. A training process allows the neural network to learn relationships between input data and output data. (For a discussion of the training process and capabilities of neural networks, see Neural Computing [22] or any other of many books on the subject.) In essence, the neural network learns to act like the numerical model running “forward” or even “backward”. The application of neural networks for intelligent control is beneficial for two reasons. First, neural network prediction is much faster than numerical model prediction. Neural networks can give a prediction of autoclave cure in less than a second, while such a prediction would take hours from numerical models. Second, neural networks can learn inverse relationships: Given a desired outcome, neural networks can provide a direct estimate of the proper processing parameters to achieve that goal.

Both controllers utilize descriptive indicators of the state of a composite during processing: degree of cure, degree of compaction, and viscosity. These can be monitored through ultrasonic techniques [23]. Degree of cure may be described as the proportion of crosslinking a thermosetting resin has undergone. Crosslinking reactions are exothermic, often leading to thermal runaway (temperatures increasing above the heater temperature to a point when degradation of the polymer occurs). Accordingly, degree of cure may also be thought of as the quotient of heat given off during cure up to a certain time over the total heat of reaction. Degree of compaction refers to the thickness of the composite. Prepreg tape always contains excess resin that must be forced out during autoclave cure: the less resin, the more compacted the composite, the better the composite properties (more resembling that of the fibers). Viscosity is an important parameter because the bulk of compaction occurs when viscosity is low and resin flows more readily. Final void content of the composite is also related to viscosity. The three quantities of degree of cure, degree of compaction, and resin viscosity describe the state of the composite at all times, and are very useful for control purposes.

Both of the developed controllers focus on specifying autoclave temperature and pressure during processing. Since no simple relationship between autoclave temperature and final part quality has been developed, and since autoclave temperature may vary continually during processing, autoclave temperature is controlled through the use of neural networks.
Olivier et al. [24] imply a straightforward relationship between autoclave pressure and final part quality of carbon/epoxy composites. Through experimentation, they found that the final void content of produced composites decreases asymptotically as autoclave holding pressure is increased. Additionally, they found that minimum final void content is obtained when pressure is applied just after resin viscosity reaches a minimum. Accordingly, the control of pressure during this study was accomplished through a simple rule: Pressure is applied at the level determined by the prepreg manufacturer after resin viscosity reaches a minimum value. The magnitude of pressure application determined by the prepreg manufacturer is deemed sufficient to provide adequate compaction and void dissolution.

3.3.1 “Forward” Controller

One controller utilizes a “forward” neural network, trained to predict exactly what the numerical model predicts. Input to the neural network includes indicators of the current state of the autoclave and composite (Figure 14): 1) heater temperature, 2) average resin degree of cure, 3) average resin viscosity, 4) degree of compaction, 5) average temperature within the composite, 6) rate of change of temperature within the composite, and 7) cure rate. Given this information along with 8) the heater temperature adjustment to be applied over the next time step, the neural network predicts the cure indicators at the end of the next time step: 1) average degree of cure, 2) average resin viscosity, and 3) degree of compaction.

The learning process for the neural network is time-consuming. Initially, the numerical model generates numerous sets of data from several process simulations. Care is taken to ensure that the generated data represents the variety of possible values the controller will see during an actual autoclave process. The neural network is shown the data until it successfully associates inputs with outputs. The neural network is then tested on an unseen data set to assess its performance. When its performance is optimized, learning is complete. The neural network may then be applied to the actual process.

A diagram of the iterative control process which determines the appropriate HTA over the next time step is shown in Figure 15. This control algorithm requires the determination of weights representing the relative importance of each of the monitored parameters during all stages of cure. Since the importance of each parameter varies continually during cure, this is not a straightforward determination. Inaccuracy of the determined weights reduces the accuracy of the “forward” controller.

3.3.2 “Inverse” Controller

The other controller exploits the ability of neural networks to learn inverse relationships. In the “inverse”
control algorithm (Figure 16), a neural network (Figure 17) is trained to give a direct estimate of the appropriate HTA. This avoids the iterative process necessary with the "forward" controller.

The "inverse" neural network is trained on the same data as the "forward" neural network, but in a different format. The neural network learns to perform like a numerical model running backward. It should be noted that prediction for the "inverse" neural network is more complicated than for the "forward" neural network, for there is a less direct relationship between input and output. Thus, the accuracy of the "inverse" neural network is expected to be less than the accuracy of the "forward" neural network.

Necessary to both control algorithms is a desired set of data giving desired numerical values for degree of cure, resin viscosity, and degree of compaction at all times. This data set may be determined in the following manner: First, run the numerical model with the manufacturer-defined cure cycle and plot the monitored variables. Then, modify the generated plots so as to produce composites of high quality in minimum cycle time.

3.3.3 Performance Testing

Back-propagation neural networks for each controller were trained to yield their optimum predictive capabilities. Then, both neural networks were tested on data generated by the numerical model. The test consisted of feeding the neural network the required inputs and noting how closely the neural network predicted the correct output (as given by the numerical model).

The "forward" neural network was found to predict values for degree of cure, degree of compaction, and the natural log of viscosity very well during the entire cure cycle. Root-mean-squared (RMS) errors were calculated from neural network testing on ten trial cure cycles and were found to be low: 0.0093 for degree of cure, 0.016 for degree of compaction, and 0.13 ln(Pa·s) for viscosity, the magnitude of error not varying appreciably with extent of compaction. According to the results of preliminary testing, the accuracy of the "forward" neural network appeared adequate for control purposes.

The "inverse" network produced more error than the "forward" network. HTA was allowed to take on integer values between -5 and 5 °C/min. As such, the neural network output was rounded to the nearest integer for control purposes. The "inverse" neural network was tested on ten trial cure cycles. RMS error from the neural network throughout the entire cure cycle was 1.00 °C/min. Neural network predictions were concluded to be much more accurate before complete compaction than at complete compaction. The RMS error at degrees of compaction less than 1.0 was
0.40 °C/min, while the RMS error at complete compaction was 1.37 °C/min. Even though diminished accuracy was obtained at complete compaction, the neural network provided a good estimate of the proper HTA for any given time step.

The “forward” controller utilizes a more complicated control algorithm, requiring an iterative process to determine the proper HTA. The iterative process requires the specification of weights representing the relative importance of the three monitored variables throughout cure. A C program was coded to determine numerical weighting constants, utilizing a factorial design of experiments approach. Weights determined by the search program are shown in Table 1. Results obtained from ten trial cure cycles with these weights yielded a total RMS error of 1.67 °C/min, an RMS error before complete compaction of 1.34 °C/min, and an RMS error at complete compaction of 2.36 °C/min. Although the “forward” neural network was found to be more accurate than the “inverse” neural network, the performance of the “forward” controller was found to be worse than that of the “inverse” controller.

Table 1: Weights Representing the Relative Importance of Parameter

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<tr>
<th>Stage Number</th>
<th>Stage 1 (δ=0)</th>
<th>Stage 2 (0&lt;δ&lt;1)</th>
<th>Stage 3 (δ=1)</th>
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4.0 SUMMARY AND CONCLUSIONS

First, fatigue crack propagation behavior of epoxy-matrix composites reinforced with either glass spheres or short glass fibers was investigated using linear elastic fracture mechanics. FCP resistance improved with the addition of either type of filler, however, short glass fibers were more effective than glass spheres. Microscopy studies indicate that more bridging occurred in the fiber filled system. Matrix-filler adhesion did not significantly affect FCP behavior under dry conditions; however, adhesion was an important factor when the epoxy matrix was saturated with moisture. Microscopy studies indicate that more matrix shear yielding occurred at crack tips when the matrix-filler adhesion was poor. These results suggest that maximum toughness is achieved when poorly bonded fibers are used to reinforced an epoxy resin that is plasticized with moisture.

Secondly, composite design procedures were investigated, and were discussed in detail with respect to two general types, namely adhesion and geometry related design aspects.

Finally, in the current study, two neural network based control algorithms and explored their applicability to the autoclave process were developed. The developed controllers differ from previous controllers in that fewer assumptions about temperature variation during the autoclave process were included, while more aspects of final part quality were considered. Therefore, the present controllers are more broad and complete than previous controllers.

Both control algorithms accomplish the same goals: to provide an estimate of the proper heater temperature adjustment at discrete time steps, and to control autoclave pressure based on the monitoring of resin viscosity. The ultimate goal of this study is the development of a controller, which guides the autoclave to consistently produce high-quality composites. Considering this goal, the “inverse” controller is the most promising for two reasons: 1) prediction speed is greater and 2) controller accuracy is much greater.

Future efforts are being directed toward applying the developed controllers to actual experimental autoclave processes. Products will be created utilizing off-line and on-line control, and total quality will be evaluated, allowing assessment of the applicability of the developed controllers to the autoclave process.
5.0 ACKNOWLEDGEMENT

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Finally, the controller design was based on research conducted by Demirci [25]. NeuralWorks Professional II/Plus v. 5.0, from NeuralWare, Inc. was applied for the creation of neural networks throughout this study, and the work was funded by the Presidential Faculty Fellowship Program of the National Science Foundation (grant number DDM-9350209). The support of Drs. Kesh Narayanan and Bruce Kramer at the National Science Foundation is greatly appreciated.

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APPENDICES

Nomenclature

$\alpha$ – degree of cure
$\mu$ – viscosity (Pa·s)
$\delta$ – degree of compaction
$T$ – temperature (°C)
$\Delta(\cdot)$ – change in quantity per minute
$(\cdot)_{avg}$ – quantity averaged throughout composite
$(\cdot)_t$ – quantity at present time step
$(\cdot)_{t+1}$ – quantity at succeeding time step
$\Delta T_{poss}$ – possible heater temperature adjustment (°C/min)

John P. Coulter is Professor and Associate Dean at the P. C. Rossin College of Engineering and Applied Science of Lehigh University. He is formally a member of the Department of Mechanical Engineering and Mechanics where he is involved in material processing, manufacturing science, and intelligent material systems research. He received his bachelor’s, master’s and doctoral degrees in mechanical and aerospace engineering from the University of Delaware in 1983, 1985, and 1988 respectively. His graduate work was in the areas of thermal and fluid sciences, composite materials, and manufacturing. Prior to joining the faculty at Lehigh in 1990, Dr. Coulter served as Senior Research Engineer and project leader of the adaptive structures research effort at Lord Corporation. He is currently responsible for all undergraduate and graduate manufacturing science components of the Lehigh mechanical engineering curriculum. As an Associate Dean, he is also responsible for all graduate study and research programs in the College of Engineering.

Dr. Coulter holds three patents, and has authored over 100 professional technical publications. He has also organized several international workshops and symposia related to intelligent material processing, and serves on the editorial board of The Journal of Material Processing and Manufacturing Science. He has received numerous research and teaching awards while at Lehigh, including both National Young Investigator (NYI) and Presidential Faculty Fellowship (PFF) awards from The National Science Foundation.

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<td>John W. Chianis</td>
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<td>Materials and Manufacturing and Design Issue Associated with Composite Products for Gas and Petrochemical Industry</td>
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<td>John P. Coulter, Joachim L. Grenestedt and Raymond A. Pearson</td>
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