

# Polymers For Extreme Service Conditions

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The field of polymer chemistry is somewhat different from other areas in chemistry because the products of polymer research and development are almost always sought with an immediate use in mind. The principle need then for the polymer is to maintain its design properties over the expected useful lifetime of the product. That means that a strong material is expected to stay strong; a stiff material is expected to maintain its stiffness (or modulus); a flexible material must maintain its flexibility, and an adhesive, its adhesion and so on.

The great problem, of course, with polymers is that they are, for the most part, organic molecules and are very susceptible to forces which cause these properties to change. These forces bring about a change in one or more of several ways. Chemically speaking this can occur by changing the molecular weight of the polymer, particularly and most usually by scission of the backbone, thereby decreasing the molecular weight commensurate with a decrease in strength, modulus, etc.

Another way that this degradation can take place is by a cross-linking mechanism where the backbones are not only tied to one another but also the effective molecular weight is increased and the material actually becomes stronger or stiffer to the point of brittleness. Accompanying this cross-linking reaction is also a shrinkage.

A third way that changes can occur at the molecular level is for the forces acting on the polymer to cause a change in functional group along the backbone or pendant to the backbone. For example polyvinyl chloride realizes a loss of hydrogen chloride and subsequent stiffening and darkening of the product. Other functional groups can undergo hydrolysis, oxidation, or photo-oxidation to introduce hydroxyl or carbonyl groups which cause other degradation processes.

So, the problems with stability in polymers is bad enough for the common cases but even more severe when one attempts to place organic or organometallic materials in unusual situations, for example, those where an extremely long lifetime is required or extreme oxidative, reductive, or hydrolytic resistances are necessary.

Stability can be brought about in two ways; one is by the addition of stabilizers. This is a common approach for the stabilization of commercial plastics against processing, aging, and weathering, for example. There are several additives known to absorb ultraviolet light and thereby stabilize plastics against outdoor aging. The use of additives for commercial plastics will not be pursued here. Instead this discussion will center around unusual circumstances in which plastics have been used or are being sought and where the stability is built into the polymer backbone in a chemical fashion rather than by a physical mixture of stabilizing agents.

The areas of use which will be discussed here are only three in number, but they vary in the destructive forces which act on the polymers. One of the first encountered by polymer chemists is the aerospace use of polymers. As seen in Table 1, there are several properties which were desired to be filled by polymeric materials. One of these is the strength-to-weight ratio. There are several polymers which can demonstrate a high strength and modulus and an extremely low density, both factors of course which are important in this particular application. Another need for this type of use is, of course, thermo-oxidative stability, one of the most difficult properties

to retain while maintaining a processability. Still other requirements for this application are adhesion and ablation (where a polymeric coating is consumed in a high energy reaction thereby removing thermal energy from the surface of a spacecraft). All of these, of course, are generally intended for a short-term use so that aging phenomena usually are not a consideration. As can be seen from the above, the types of detrimental or degrading forces experienced by polymers in aerospace use are temperature, oxidation, environmental water (which has a long term effect particularly in composites and adhesive joints), and high stress situations which tend to accelerate degradation.

The second use of polymer in extreme service is perhaps one of the newest of these and that is in the area of recovery and use of geothermal energy. Here oxidative forces are not in play, but hydrolytic, thermo-reductive resistance is necessary. Also this application is generally a short-term one, or at least it can be, in many of the down-hole applications. It is different from the aerospace use also in that these materials are commonly elastomeric as seals in either static or dynamic applications. The types of forces which must be resisted by these polymers are high temperature, hydrolysis, chemical reduction, salt, hydrogen sulfide, and abrasion.

The last application which will be addressed here is that of undersea uses of polymers. In this case the degrading of forces are not so extreme; however, those that are present must be withstood for very long periods of time; 15 years is not at all uncommon. This application then puts a whole new type of stress on the polymer and is one where aging becomes significant and, of course, where accelerated aging techniques can be applied. Properties that are sought for this type of application are adhesion, low permeability, corrosion prevention, and marine growth resistance. Perhaps the two forces which are acting most strongly here are hydrolysis and time.

## Aerospace-Thermo-oxidatively Stable Polymers

The use of polymeric materials, which are mostly organic, is an inherently difficult task when one is seeking thermo-oxidative stability. Organic compounds almost always melt below 250° C and certainly undergo severe oxidation below 300° C. It seems that organic backbones would be a poor choice where this kind of stability is needed. In fact, great strides have been made in overcoming these problems, even with the use of a totally organic systems. One of the first tasks facing researchers in this area was to define which functional

Table 1. Applications, Properties, and Detrimental Factors

	Aerospace	Geothermal	Undersea
Properties Needed	Strength to weight ratio Adhesion Modulus Ablation Thermal Stability	Hydrolytic and Thermoreductive Resistance Elasticity	Adhesion Impermeability Marine growth Resistance Corrosion prevention
Detrimental Forces	Temperature Oxidation Stress Water	Temperature Hydrolysis Reduction $H_2S$ Abrasion	Hydrolysis Time

groups have this inherent thermo-oxidative stability and which ones are weak in this regard. The weak ones are commonly alkyls, amines, and alcohols while strong ones are aromatic, ether, sulfone, and heterocyclic and several inorganic or organometallic systems such as siloxane, phosphonitrile, and carborane. So the task becomes one of removing weak links and providing strong bonds such that the final product is tractable.

If one considers the thermal stability of newly-discovered polymers versus their year of discovery (1960–1980), it is obvious that thermal stability was obtained early in this research. Such a comparison does not show how soluble, moldable, or processable these materials were. The first 5 to 10 years was concerned mainly with the synthesis of new types of materials seeking primarily thermo-oxidative stability. Later, research was directed toward the production of the materials that were not only stable but also processable and, therefore, usable. The general goal sought by researchers in this field was to have a material which would maintain its physical properties at 250° C for extended periods (several thousand hours) and even up to 500° C for 1 hr. One of the constant problems which arises in designing and synthesizing thermo-oxidatively stable polymers is that desirable properties are generally in opposition to one another. Almost invariably as one develops an increased thermal stability, it is accompanied by an increase in strength, modulus, rigidity, and softening point. Unfortunately also accompanying the increased stability is lower solubility, tractability, moldability, and, in general, processability. Therefore, a tradeoff is commonly necessary where one must sacrifice some property advantages in order to get a material which is usable.

The definition of thermal stability has been an interesting but uncertain process for a use in this technology. The most common way for this to be determined in the research laboratory is by thermogravimetric analysis (TGA). TGA measures the weight loss in a sample continuously while the temperature on the sample is gradually increased.

A more realistic approach is by the use of isothermal weight loss analysis. This, of course, requires more time, material, and equipment but does provide a more realistic assessment of the ability of the polymer to retain its properties. This method of monitoring weight is made of several polymer samples at different temperatures and the weight loss is followed against time.

Of course, even isothermal data are not completely realistic. The only way to look at a situation for a particular polymer is to create the mechanical application (stress) and thermo-oxidative environment which the material will see in use. There are, of course, real dangers in trying to use just one method of stability determination. Consider the following data for just two polymer types. The numbers following each of these types represent thermal stability by TGA in air, maximum use temperature for 10 min and maximum use temperature for 200 hr.: polyimide, 554°, 377°, and 358° C; polybenzimidazole, 454°, >650°, and 320° C. So one can see that there is little or no relationship between the methods of thermal analysis for any one polymer system and certainly not one that is comparable between two different backbones. A

relatively recent revelation is that indeed the comparison of thermal stabilities of polymers is very difficult even between those similar structures. The difficulty arises because of different degradation mechanisms which might apply, residual functional groups which may lead to change scission or cross-linking, incomplete reaction of the monomers, or residual species that may promote degradation.

The following discussion will consider some specific examples of successful, thermally stable polymers.

### Heterocyclic Polymers

#### Polybenzimidazole (PBI)

The study of heterocyclic systems was first done with some success by Professor C. S. Marvel and his co-workers, when aromatic polybenzimidazole (PBI) was synthesized in the late 50's and early 1960's (Fig. 1). This material has in the ensuing 20 years undergone considerable development and will be prepared in large (million pound) quantities beginning in 1982 by Celanese Corporation. The general synthetic route and structure of the polybenzimidazoles is given in Figure 1 and shows the condensation of a diacid or diacid derivative with a tetraamine. A two-step process occurs where the first step is loss of a by-product to give the amic acid intermediate. The second step then is complete cyclization to the benzimidazole function. The amic acid intermediate is an important one because the final product is relatively intractable; however, the intermediate is soluble and can be processed to films or fibers in which state the second cyclization step takes place.

A phenomenal number of benzimidazoles have been synthesized with as many as 15 tetraamines and 60 dicarboxylic acids.

With PBIs some of the standard relationships are seen which are typical of these types of materials, namely: (1) aromatic nuclei are more stable but less tractable than aliphatic ones and *para*-substitution provides more stability but less tractability than *meta*; and (2) any flexibilizing groups such as ether or sulfone linkages between aromatic rings do indeed increase flexibility and solubility but lower the thermo-oxidative stability somewhat. Polybenzimidazoles have shown good adhesion to glass when cast from a solution, a property which dictates use in glass composites, laminates, and filament wound structures. Fibers can be wet-spun, heat treated to result in a deep gold color, and woven to cloth. This cloth is used as a flame resistant clothing or in applications where an expensive but unusual material is needed, such as high temperature filter bags for industrial processes. There are, in addition, several serendipitous discoveries with PBI as with other materials. For example, PBI fibers show promise as reverse osmosis membranes as do several of the backbones designed for thermal stability. They can also be pyrolyzed to produce graphite fibers which demonstrate high strength and high modulus for use in composites. Still another use is as battery separators. PBI can also be fabricated as a foam which gives a high char yield which demonstrates a considerable insulation resistance.

#### Poly(Phenyl Quinoxaline) (PPQ)

The PPQs have been an interesting polymer not only because of the properties which they demonstrate but also because of the potential use of these materials. A very strong application for PPQs was an adhesive for the supersonic transport (SST) program. The original polymer was synthesized concurrently by Stille and Williamson in the United States and by de Gaudemaris and Sillion in France. The phenylated version was prepared by Hergenrother and Levine. This last development, that is the production of a material with pendant groups, was an important one because it led to a soluble, processable product.

The synthesis of PPQ is shown in Figure 2 which shows a condensation between an aromatic tetraamine and a bis-

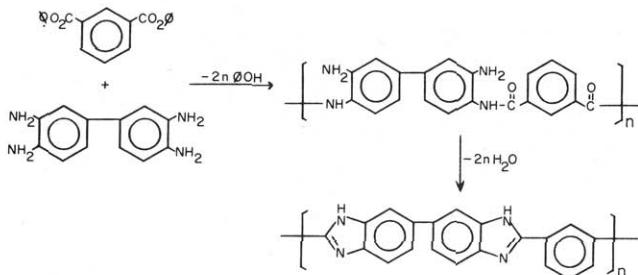


Figure 1. Synthesis of aromatic polybenzimidazole (PBI).

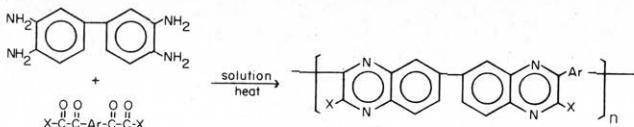


Figure 2. Synthesis of poly(phenyl quinoxaline) (PPQ).

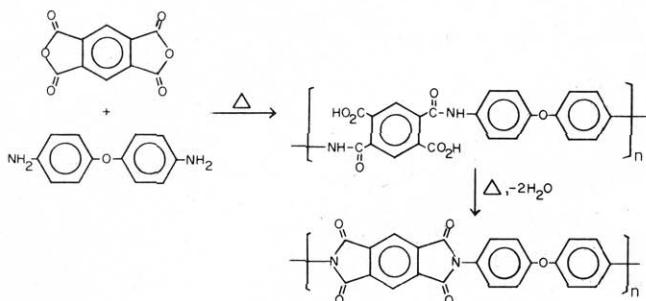


Figure 3. Synthesis of polyimide.

glyoxal. One can recognize that one of the difficulties here is the synthesis and purity of the starting materials. However, molecular weights range up to 300,000, glass transition temperatures ( $T_g$ ) up to 370° C, polymer softening temperatures up to 350° C, and solubility in meta-cresol chloroform and tetrachloroethane. From a meta-cresol solution one can cast tough, flexible, yellow films. Thermal oxidative stability by TGA shows to be in the area of 500° C.

The applications of these materials include laminates with glass, boron and graphite fibers and adhesives on stainless steel and titanium.

### Linear Backbones

#### Polyimides

Polyimides (Fig. 3) have one of the longest histories of any class of materials in the thermo-oxidatively stable area. These materials are synthesized by the condensation of dianhydrides and diamines by the process shown below.

The most common of the multitude of polyimides is that structure from pyromellitic dianhydride and diaminodiphenyl ether. This and similar materials have been marketed under the names Kapton® (formerly H-film, Dupont), P13N (TRW), QX-13 (ICI), and Kinel® or Kerimid 601® (Rhone-Poulenc). This polymer shows a stability up to 500° C (5% weight loss for 15 hr) by isothermal testing in an inert atmosphere. Even in air the stability is maintained to 425° C. By TGA, data up to 580° C are obtained.

Polyimides are available as pre-cured films, fibers, curable enamels, adhesives, and composites resins. Furthermore, they have shown some utility as reverse osmosis membranes but only after the incorporation of a polar function onto the backbone to increase the association of water.

As can be seen from the above equation, water is an off gas in the polymerization which can interfere with the behavior of the final product as a laminate or adhesive. Therefore, one of the common methods now used with several types of backbones is to produce low molecular weight with terminal cross-linking functions, such as acetylenic groups. Such a material is Thermid 600® (Gulf) which, while soluble and therefore processable, can be thermally cross-linked and permanently formed and made even more heat stable.

#### Polyamides

Perhaps the largest group of thermally stable polymers is the polyamides. This is due not only to their success in practical applications but also to their relative ease of synthesis,

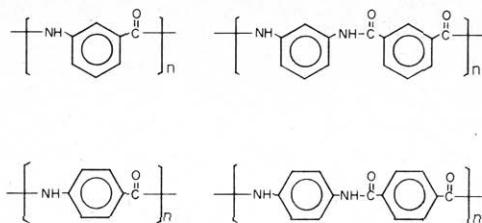


Figure 4. Polyamides.

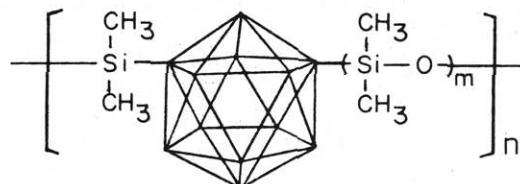


Figure 5. Carborane-siloxane.

requiring the condensation of diacid derivatives with diamines. The aliphatic versions are known as nylon and the aromatic versions are now known as "aramids." Of course the aromatic type of backbone is less tractable than the aliphatic but much more thermally stable and much higher in modulus and strength. The term "aramid" has been assigned by the Federal Trade Commission to mean a polyamide in which at least 85% of the amide functions are attached directly to aromatic rings.

Polyamides (Fig. 4) can be made in at least two general ways. One is the condensation of an acid amine (AB type of monomer) or by the co-condensation of a diacid (AA monomer) with a diamine (BB monomer) to give an AA-BB type of polymer.

Several commercial names are available for these aromatic polyamides. One is Nomex® (Dupont) which is essentially a polyamide with *meta* catenation, that is from the condensation of isophthalic acid and *m*-phenylene diamine. This product has a use temperature of 370° C and shows stability by TGA of 450° C. It is used to produce flame and heat resistant cloth. In order to provide additional strength a newer product, Nomex II® is produced by the addition of a few percent of Kevlar® which is a chemical structure similar to Nomex® but with *para* catenation.

The properties of the para-oriented aramids, namely the one of extremely high modulus, has brought about its use as a composite filler, electrical insulation and high speed bearings. Other properties which contribute to the advantage of such materials are low density, low conductivity, low corrosion, and high strength to weight ratio, especially when compared to possible metallic competitors.

### Organometallic Polymers

One of the areas of research which has been neglected somewhat by polymer chemists is that of the formation of inorganic or organometallic backbones. There is only one very well known material and this is polysiloxane, which has a silicon-oxygen alternating function composing the backbone and two aliphatic or aromatic groups pendant to the silicon. Two other examples of inorganic chains will be presented here which are not as well known but are in advanced commercial development.

#### Polycarboranes

In the mid-1960's Olin Matheson and Princeton Laboratories made known their research of a backbone which contained the ten-boron, two-carbon cage, and siloxane functions (Fig. 5). This material was first marketed under the name Dexsil® and later under the name Ucarsil® by Union Carbide, but at a premium price (\$2,000 to \$4,000 per pound).

These products are referred to as SiB-2 or SiB-4 where the integer refers to the number of siloxane functions separating the carborane cages. A designation 10-SiB is also used to signify that a ten-boron, two-carbon cage is used, that is, decaborane, rather than a smaller cage of 5 borons.

The actual commercial product has a vinyl end-cap which provides a site for peroxide cross-linking to an elastomer which is commonly filled with talc or silica. These polymers have very low glass transition temperatures, -32 to -60°C, and thermal stabilities up to 425°C and 540°C. However, beginning at 275°C the carborane undergoes oxidation, which in fact means that it gains weight, therefore diminishing the value of the weight loss data taken in air.

### Polyphosphazenes

Polyphosphazenes were first discovered at Pennsylvania State University, developed further by Horizons, Inc., and brought to commercial application by Firestone. This material (Fig. 6), called an inorganic rubber, is a broad temperature-range elastomer and is fire resistant.

The polymers are synthesized by the ring opening reaction of hexachlorocyclotriphosphazene and subsequent substitution of the labile phosphorus chlorine bond with alkoxy or alkyl amino functions.

The most useful of these, the fluorinated version, termed PNF, has an extremely broad range of elasticity from -95 to +270°C. Phosphazene polymers are usually soluble in common organic solvents such as chloroform or THF and can be formed into fibers by extrusion or films by solution casting. The fluorinated aliphatic versions must be dissolved in chlorofluoroalkanes.

One of the most recent suggestions for use of these materials is as biodegradable polymers, specifically blood compatible surgical implants which are carriers for biologically active species, that is, as a slow release substrate for implanted drug delivery systems. More pedestrian uses are wire coatings and flame retardants for foams.

### Miscellaneous

This brief review can only touch on the hundreds of materials and useful application that have been uncovered during the research for thermally stable and processable materials. Several other of these structures and names and properties are given in Table 2.

**Table 2. Examples of Other Thermo-Oxidatively Stable Polymers**

Name	Structure	Notes
Poly( <i>p</i> -xylylene)		Insoluble/crystalline. mp 300–400°C. Forms coating by vacuum vapor deposition. Oxidizes above 100°C.
Polyester		Use temperature 325°C. Fabrication by compression sintering. Crystalline. Insoluble. High flexural modulus.
Poly(phenylene ether), PPO		Self-extinguishing. HDT 100–150°C. Tg 90–220°C. Tm 262–484°C.
Polypyromellitimides		Soluble. Stable to 340–650°C in N2.
Poly-1,3,4-thiazidazole		Flexible, films and fibers. Stable to 400–600°C. More tractable than oxo analog.
Poly(benzimidazobenzophenanthroline) ladders (BBL) [or poly(imidazoisoquinoline) ladders]		Slightly soluble. Tg 500°C. Stable to 450–500°C or 200 hr at 370°C in air. Forms supramolecular aggregate films.

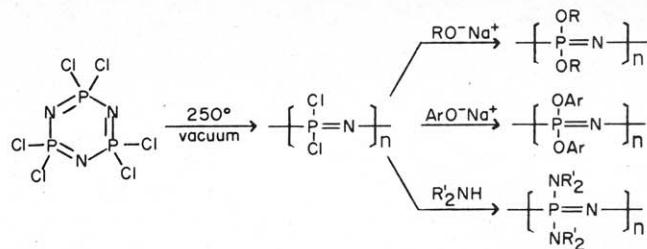


Figure 6. Synthesis of polyphosphazenes.

### Geothermal Applications

#### Elastomers

The recovery and use of geothermal energy would appear to be a rather straightforward view of the fact that well-drilling technology is thoroughly developed. However, several unexpected problems have arisen in seeking thermally stable elastomers for down-hole operations. One of the conditions which these materials must meet is, of course, a thermal stability. Another condition is hydrolytic stability and still others are a resistance to abrasion, hydrogen sulfide, and gas absorption. Another interesting phenomenon generally new to the polymer chemists is that these applications require only small quantities of very specialized materials. As a result, what would be considered outrageous costs for these materials are not at all out of the question.

Initially the standard approach was to provide materials for geothermal well conditions. This included surveying the literature of thermally stable polymers, seeking out the most probable candidates, and either testing or modifying them so that they might become suitable materials. At this point generally a great surprise was registered when the discovery was made that the aerospace stable materials failed catastrophically in geothermal applications. It is obvious now that aerospace materials were thermo-oxidatively stable and geothermal needs were those of thermohydrolytic-reductive stability. For example, silicone, carborane, and phosphazene polymers, considered to be very promising candidates, showed no resistance whatsoever to simulated test conditions. An

example of test conditions is 300 ppm H<sub>2</sub>S, 25,000 ppm NaCl, 1,000 ppm CO<sub>2</sub>, oil and water, 260° C, and 5,000 psi for 24 hr with mechanical stresses applied. An additional problem is that due to the extreme conditions of use, the accelerated testing is impossible.

The testing and evaluation program looked at many materials and eventually focused on modified commercial elastomers which showed the greatest promise: ethylene-propylene terpolymer (EPDM) nitrile rubber (Buna-N) and fluorinated elastomers, (Viton® and Aflas®). Viton® is a copolymer of vinylidene chloride and hexafluoropropylene while Aflas® is an alternating copolymer of tetrafluoroethylene and propylene.

Other attempts to produce stable products have been made. One of these is the production of a high glass transition temperature material which at ordinary temperatures may be rigid but at use-temperature in the geothermal well becomes elastomeric. The approach here was to produce a polymer with rigid blocks of PPQ incorporated with blocks of polystyrene. The latter which will soften at use temperature. Limited results were realized.

An attempt was made in order to allow marginally stable materials to be used as O rings. This approach was to apply a resistant service coating such as a fluorinated polymeric material. This would accomplish two purposes: (1) to decrease the access of the chemically degrading species to the elastomer, and (2) to provide a low friction and abrasion-resistant surface. The production of a 400A° coating of fluorinated polyethylene was made to Kalrez® and Viton® (both fluoropolymers) and some small improvement was possible.

### Polymer-Concrete Composites

Another way to use the polymers in geothermal applications is to use them in a composite mixture with polymer. Two methods are possible. One is the impregnation of dry, cured concrete with a low viscosity, liquid monomer followed by a cure of the polymer; the second is to mix the aggregate with monomer and polymerize the mixture in a mold, as would normally be done for Portland cement. The latter has been shown to be of value for geothermal plants while the former has been applied to concrete roadways and bridge decks to seal the surface from salt and water and subsequent freeze thaw effects.

To provide a system which can be mixed and cured in a mold, silica sand and Portland cement are used as solid particulate fillers in a monomer mixture consisting of 50% styrene, 33% methyl methacrylate, and 17% trimethylolpropane trimethacrylate. This composition has given no failures in field tests which have been in existence for over 2 years at 240° C. Furthermore, they have withstood 200° C in hydrochloric acid for 170 days with no evidence of deterioration.

### Undersea Application

The last unusual condition to which polymers have been subjected is not one which imposes extremes in temperatures or chemical attack but instead one of the most severe reagents of all-time. Long-term maintenance of properties such as adhesion and low water permeability are critical. Elastomers are used to isolate undersea electronic devices, such as sonar transducers and hydrophones, which must maintain their integrity for a long period of time, perhaps as much as 15 years. The forces acting on these materials are of course hydrolysis, water leaching, corrosion at the adhesive interface, marine growth, and mechanical degradation by sonic agitation.

The materials which are commonly used in systems such as these are W-type Neoprene® and butyl rubber. The former has the advantage of easier processing while the latter is superior in permeation resistance.

The ability of rubber to isolate a system from water is, of course, the key property. Water will permeate commercial Neoprene® formulations, even those up to 1/4-in. thick at an appreciable rate considering a 15-year use period. Rates on the order of 1–2 mg/cm<sup>2</sup>/day have been measured for some formulations. The permeation rate and water absorption (leading to swelling, another problem) vary considerably with the components of the rubber. For example, some additives form soluble chlorides which promote water association. A further complication is that permeability is enhanced with aging and sonic excitation.

Permeation is not the only mechanism by which water can enter. Another is failure of the metal-rubber bond. This problem area involves not only elastomer composition, processing, and cure but also primer and adhesive used on the metal. If all factors are not carefully controlled, debonding and corrosion can occur to bring about rapid electronic failure.

The one advantage that polymer and material scientists have in dealing with undersea uses is that acceleration methods can be used to predict lifetimes. Accelerated life testing (ALT) becomes important and can compress 15 years of lifetime use into a few months. Of course the acceleration is accomplished by raising the temperature, to as much as 75° C for Neoprene®, as long as the higher temperature is a valid one. For example, at 90–95° C Neoprene® degrades by mechanisms which are not present at 20° C so the acceleration is not realistic.

Great advances are now being made in development of commercial materials for undersea applications and in accelerated test methods to predict long-term life expectancy.

### Conclusions

In the past twenty years polymers have been applied successfully to several difficult uses. New polymers have been synthesized and commercial materials have been developed to withstand high temperatures, oxidation, reduction, hydrolysis, and long exposure times to seawater.

Still other extreme or unusual applications are being made: high modulus fibers for tire cords, reverse osmosis membranes for water purification, degradable sutures, and slow or controlled-release materials for drug, fertilizer, pesticide or herbicide delivery.

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