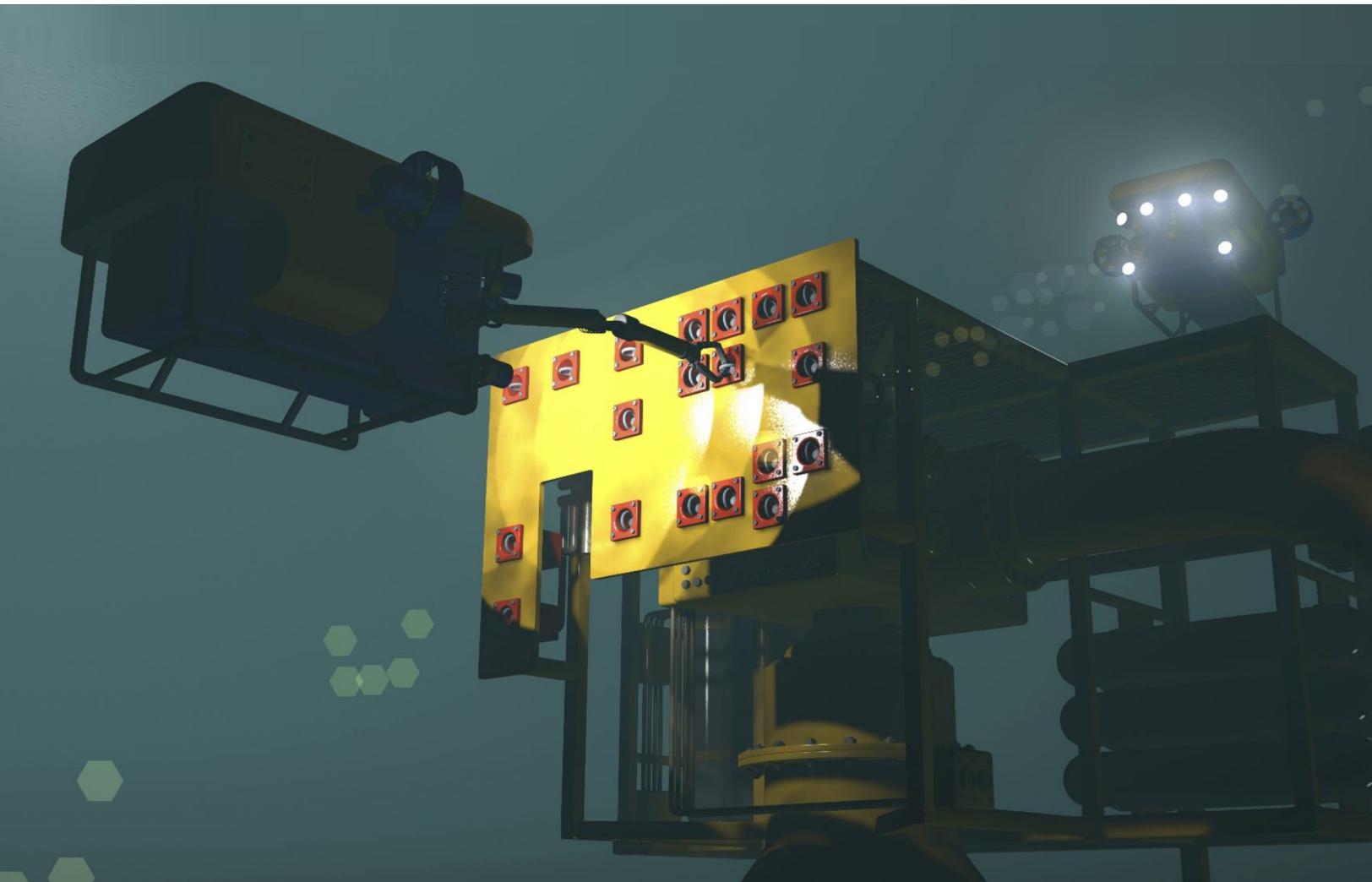


Technical Research Report

The Effect of Water Absorption During Deep Ocean Submersion on the Mechanical Properties of Engineering Plastics and Composites – an Experimental Investigation

Röchling Engineering Plastics and Curbell Plastics, Inc.



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Abstract

Engineering plastics and composites are being used for an increasingly wide range of deep-ocean devices including remotely-operated underwater vehicles, marine-grade electrical cable connectors, and undersea sensors. The mechanical properties and water absorption characteristics of polymers in shallow water with low hydrostatic pressure are well understood. However, it is essential to understand how these properties are affected by long-term submersion in seawater at depths greater than 1 kilometer with high hydrostatic pressure if plastics are to be specified for a broader range of undersea applications. The current study immersed samples of 20 engineering plastics and composites in pressurized artificial seawater using laboratory pressure vessels, simulating the hydrostatic pressure associated with an ocean depth of 3500 meters. The mechanical properties and water absorption levels of the materials were periodically tested to detect any changes. Some polymers were largely unaffected by exposure to seawater at high hydrostatic pressure while others exhibited significant changes in mechanical properties and water absorption levels.

Keywords: Polymers; Plastics; Composites; Hydrostatic Pressure; Mechanical Properties; Water Absorption; Offshore Oil and Gas; Deep Ocean

1. Introduction

Engineering plastics and composites are lightweight, easy to fabricate, corrosion resistant, and durable, which are desirable characteristics for marine applications. A number of plastics have specific gravities that give them close to neutral buoyancy in seawater, which can be advantageous for certain undersea devices such as ROVs [7]. Some polymer materials are transparent to visible light and they are used for optical applications such as the dome covers on underwater cameras. Polymers are (to varying degrees) transparent to RF signals, which may become increasingly important for remotely controlling underwater equipment as this technology develops and is more widely adopted.

A broad range of commercial, scientific, and government activities are done in the deep ocean and thermoplastics and composites are frequently used in the equipment employed for these purposes. The oil and gas industry conducts extensive operations in marine environments and polymers are used in pipe handling and guiding equipment, undersea electrical connectors, valves, and wellhead caps. Polymers are good thermal insulators and they are often used to insulate undersea oil pipes to maintain fluid temperature and promote flow. Thermoplastics and composites are used for marine biology, oceanography, and commercial fishing applications including sensor housings and camera bodies. Many military systems are designed to operate in the ocean and polymers are frequently specified for underwater radomes, weapon system housings, electrical insulators, and seals.

1.1 The Benefits of Semi-Crystalline Thermoplastics and Composites for Marine Applications

Semi-crystalline thermoplastic materials such as UHMW-PE (ultrahigh molecular weight polyethylene), polyamide 6, and PEEK (polyetheretherketone) can be formulated to have good friction and wear properties without the use of liquid lubricants. Oils and greases may not be practical for certain marine applications since they can quickly wash away when they are immersed in seawater. Plastics are particularly useful for friction and wear applications since they result in very little wear on mating metal parts. Semi-crystalline thermoplastics have good chemical resistance and moderate compressive moduli, which allow them to conform to mating metal surfaces. This makes them ideal choices for underwater sealing applications.

Composites have high specific strength and high specific moduli, which make them good candidates for metal replacement in marine environments when corrosion resistance and good mechanical properties are required. These materials also have relatively low coefficients of thermal expansion, and high bulk moduli [7], which improves their dimensional stability when immersed in seawater at various depths and temperatures.

1.2 Purpose of the Current Study

Marine applications often involve operating at ocean depths of up to 3500 meters. The temperature is around 4 °C at this depth and the hydrostatic pressure is approximately 35 MPa (350 bar, 5076 psi). Previous research [4, 7] has stressed the importance of understanding the effects of high hydrostatic pressures on the properties of polymer materials when considering them for deep ocean applications. The purpose of the current study is to investigate the effects of immersion in seawater at elevated hydrostatic pressure on a wide range of thermoplastics and composites so that engineers will be able to make more informed decisions when selecting plastic materials for use in deep water environments.

2. Materials / Experiment

Thirteen thermoplastics and seven composites manufactured by Röchling Industrial were selected for the study. Table 1 and Table 2 show the materials and their trade names. These represent many of the commercially important engineering polymers. One of the composites, Durostone® UPM S2, was tested both uncoated and also coated with an industrial lacquer to see if the coating would affect its water absorption properties.

Table 1. Thermoplastic Materials

Röchling Industrial Trade Name	Abbreviation	Material
Polystone® P	PP	Polypropylene homopolymer sheet
Polystone® G	PE300	High density polyethylene sheet
Polystone® M	PE1000	Ultrahigh molecular weight polyethylene sheet
Sustamid® 6G	PA6, cast	Polyamide 6, cast sheet
Sustarin® C	POM-C	Acetal copolymer sheet
Sustadur® PET	PET	Polyethylene terephthalate, semi-crystalline sheet
SustaPVDF	PVDF	Polyvinylidene fluoride sheet
SustaPEEK	PEEK	Polyetheretherketone sheet
Sustatron® PPS	PPS	Polyphenylene sulfide sheet
Sustakon®	PK	Polyketone sheet
Fibracon® PTFE, Virgin	PTFE	Polytetrafluoroethylene, virgin sheet
Fibracon® PTFE, carbon and graphite filled	PTFE, 8% carbon, 2% graphite	Polytetrafluoroethylene, 8% carbon, 2% graphite sheet
Fibracon® PTFE, TFM™	PTFE, PPVE modified	Polytetrafluoroethylene, perfluoropropyl vinyl ether modified sheet

Table 2. Composites

Röchling Industrial Trade Name	Thermoset resin	Reinforcement	Shape
Durostone® UPM 203	Unsaturated polyester	Glass mat	Sheet
Durostone® UPM S2	Unsaturated polyester	Glass mat and glass fabric	Sheet
Durostone® UPM S2 coated with lacquer	Unsaturated polyester	Glass mat and glass fabric	Sheet
Durostone® EPC 205	Epoxy	Glass fabric	Sheet
Durostone® EPM S7	Epoxy	Glass mat	Sheet
Durostone® EPX-M	Epoxy	Continuous glass fiber	Filament wound ring
Durostone® UPR S19	Vinylester	Glass fabric	Sheet
Durostone® VEGMZ-LP	Vinylester	Glass mat and glass roving	Pultruded profile

Specimens of each material were prepared in accordance with ISO test methods so that the tests shown in Table 3 could be performed. Materials were not tested for a particular property when the specimen geometry required by the test method could not be yielded from the commercially available shape. For example, certain ISO test specimens can not be produced from filament wound rings or pultruded profiles.

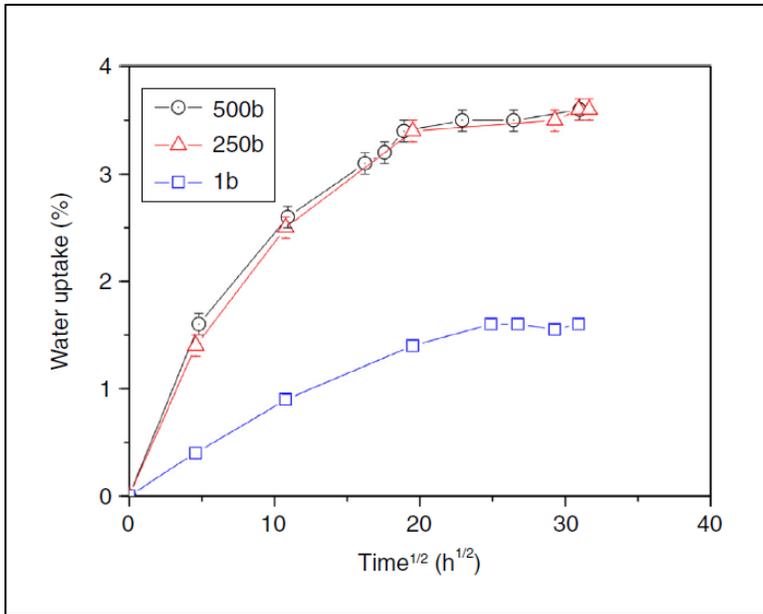
Table 3. ISO Test Methods used to Characterize the Materials

Property	Test Method	Unit of Measure
Water absorption	ISO 62	% weight gain
Tensile strength and tensile modulus	ISO 527-2	MPa
Tensile elongation	ISO 527-2	%
Flexural strength and flexural modulus	ISO 178	MPa
Charpy notched impact strength	ISO 179-1	kJ/m ²

The initial dry (below 1% moisture content) mechanical properties of each material were measured using the tests listed in Table 3. The samples were then immersed in pressurized artificial seawater with 35 PSU (practical salinity units) at room temperature for a period of 56 days using a laboratory pressure vessel. The vessel was pressurized to 350 bars to simulate an ocean depth of 3500 meters.

Testing at high hydrostatic pressure was particularly important for the composites. Previous research by Pierre Le Gac [4] showed that a glass fiber reinforced epoxy composite exhibited higher water absorption at elevated hydrostatic pressures (see Figure 1). He attributed this to the high pressure forcing water into porosity in the composite material as well as water entering at the interface between the epoxy resin and the glass fibers.

Figure 1. Excerpted from an article by Pierre Le Gac, showing weight gain from water absorption for an epoxy/glass composite at hydrostatic pressures of 1 bar, 250 bar, and 500 bar [4].



Samples of the thermoplastic and composite materials were removed after 7, 14, 28, and 56 days and placed in sealed plastic bags for shipment to the mechanical properties testing facility. The pressurized seawater immersion procedure was done at the Fraunhofer Research Institution for Marine Biotechnology and Cell Technology in Lübeck, Germany. The mechanical properties testing was done at Röchling's laboratory in Haren, Germany. Graphs showing water absorption as a function of immersion time for each material are shown in Figures 2 and 7. Graphs illustrating mechanical properties as a function of immersion time are shown in Figures 3, 4, 5, 6, 8, and 9. The mechanical property graphs shown in the figures were selected since they illustrate the most relevant behaviors of the polymers during testing.

3. Results

Figures 2 through 6 show water absorption and mechanical properties as a function of immersion time for the thermoplastic materials.

Figure 2. Water absorption as a function of immersion time for the thermoplastics

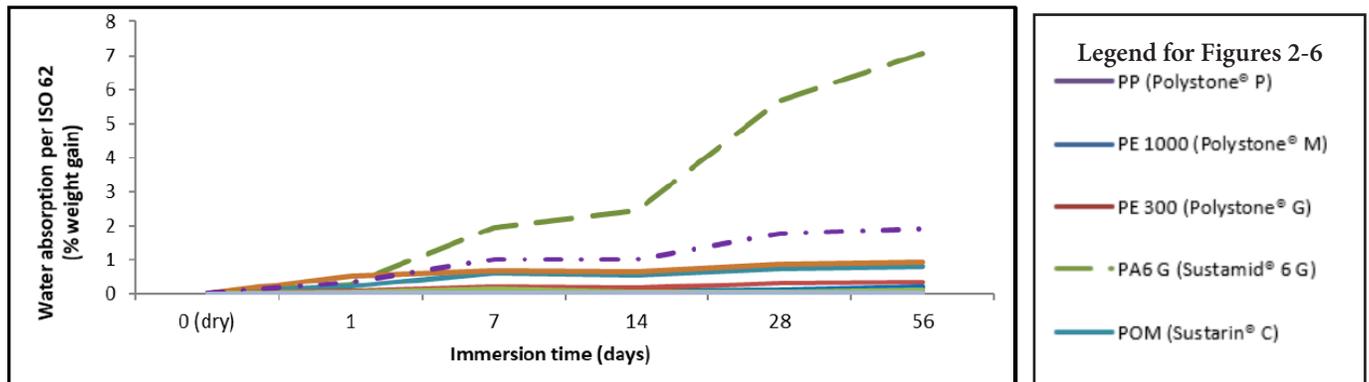


Figure 3. Tensile modulus as a function of immersion time for the thermoplastics

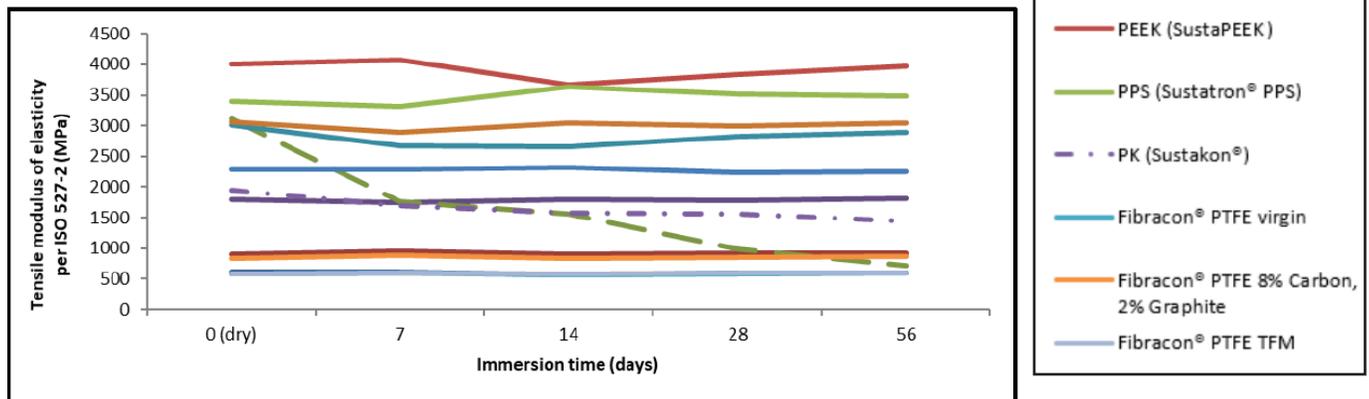


Figure 4. Tensile strength as a function of immersion time for the thermoplastics

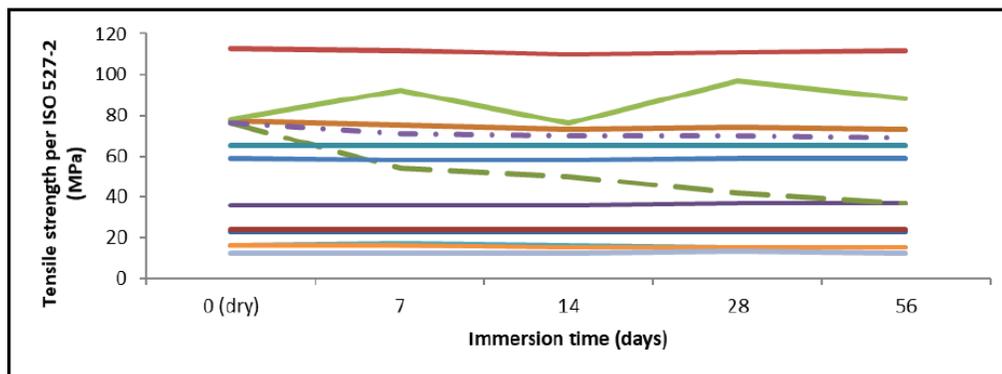


Figure 5. Tensile elongation as a function of immersion time for the thermoplastics

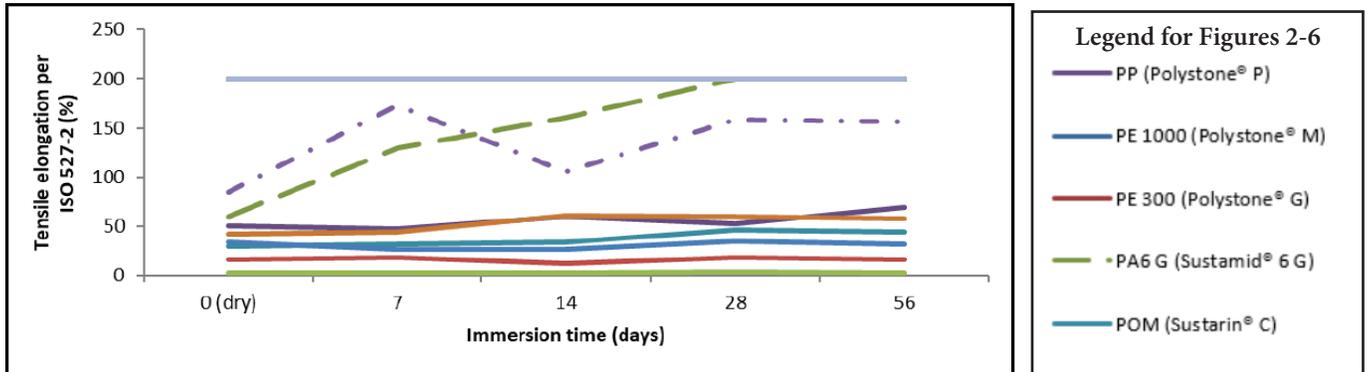
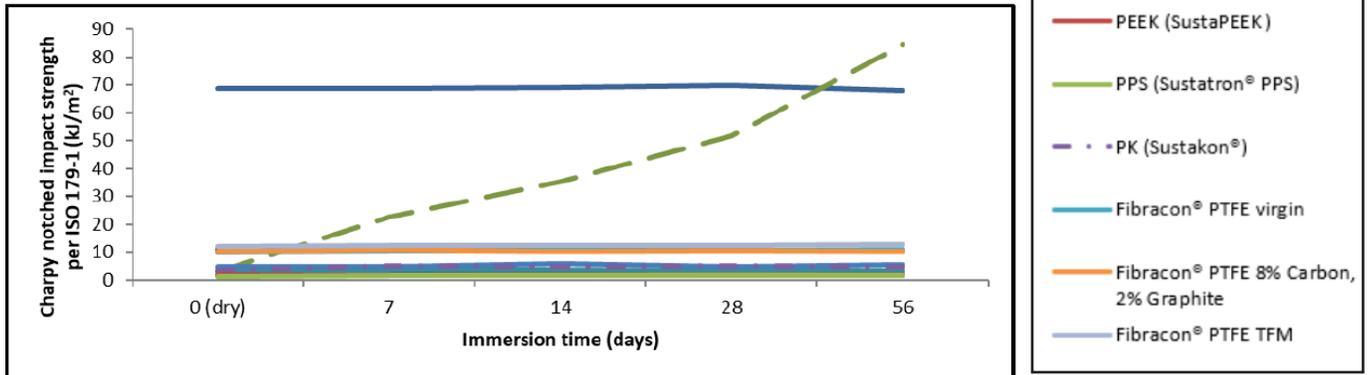


Figure 6. Charpy impact as a function of immersion time for the thermoplastics



Figures 7 through 9 show water absorption and mechanical properties as a function of immersion time for the composites.

Figure 7. Water absorption as a function of immersion time for the composites

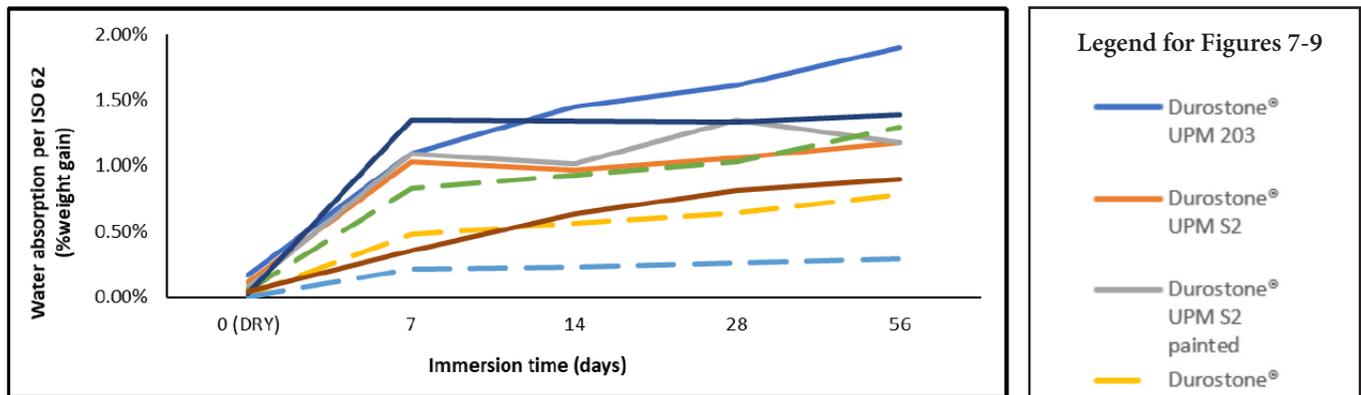


Figure 8. Flexural modulus as a function of immersion time for the composites

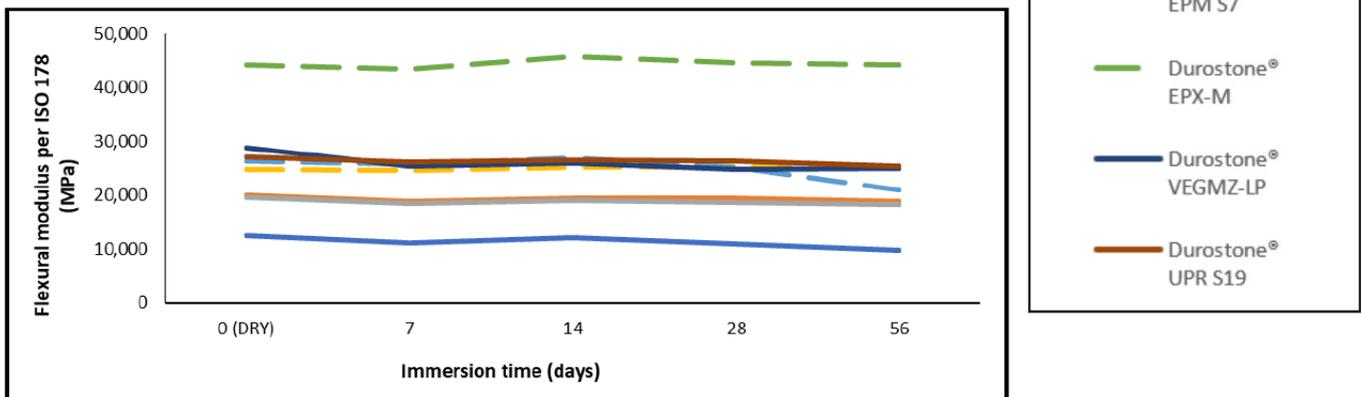
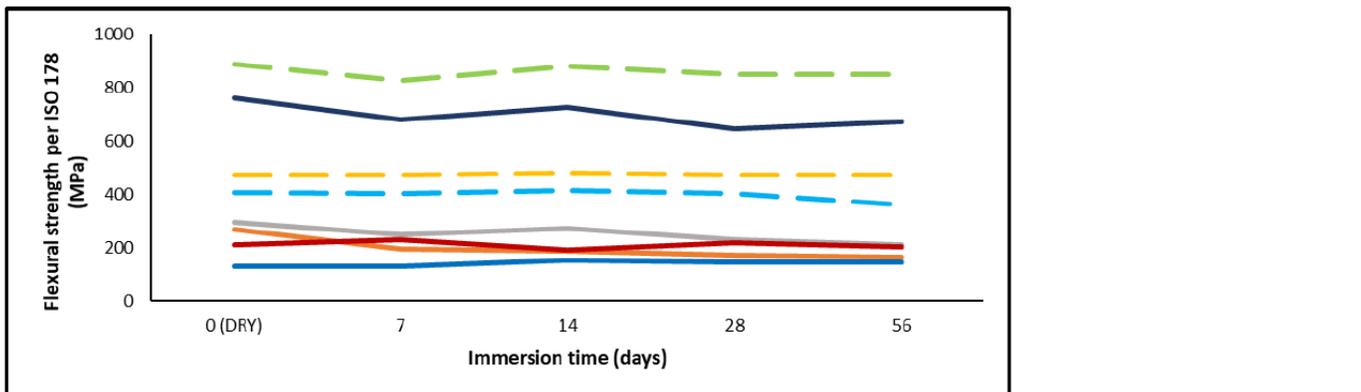


Figure 9. Flexural strength as a function of immersion time for the composites



3.1 Results for the Thermoplastics

With the exception of Sustamid® and Sustakon®, the thermoplastic materials absorbed little moisture (less than 1% weight gain) and were largely unaffected by 56 days of immersion in pressurized seawater. Sustakon® gained 1.9% weight due to moisture absorption and exhibited a 26% decrease in tensile modulus and a 9% decrease in tensile strength. Sustakon® also had a 29% increase in Charpy impact and an 84% increase in tensile elongation, indicating that the material became less stiff, tougher, and more ductile after absorbing water.

Sustamid® had the largest water absorption, gaining 7.1% weight after 56 days of immersion. Sustamid® was significantly plasticized by the absorbed water, with a 77% decrease in tensile modulus, a 51% decrease in tensile strength, and a 233% increase in tensile elongation. Sustamid® showed an increase in Charpy impact from 3.0 kJ/m² in the dry condition to 84.4 kJ/m² at the conclusion of the test.

3.2 Results for the Composites

All of the composites gained less than 2% weight due to water absorption after 56 days of immersion. The epoxy resin composites exhibited the least change in mechanical properties. Durostone® EPC 205 and EPX-M had less than 5% reduction in flexural strength and flexural modulus at the conclusion of the test. Durostone® EPM S7 had a 20% reduction in flexural modulus and a 12% reduction in flexural strength. The unsaturated polyester resin composites exhibited a greater change in mechanical properties, with some materials showing 20% to 40% reduction of strength and modulus after 56 days of immersion.

It is interesting to note that the lacquer-coated Durostone® UPM S2 unsaturated polyester/glass composite had nearly identical water absorption to the uncoated sample of the same material. This underscores the importance of carefully selecting coatings for composites used in marine applications. The coating used for this study was permeable to seawater at high hydrostatic pressure and it failed to prevent water absorption in the underlying composite substrate.

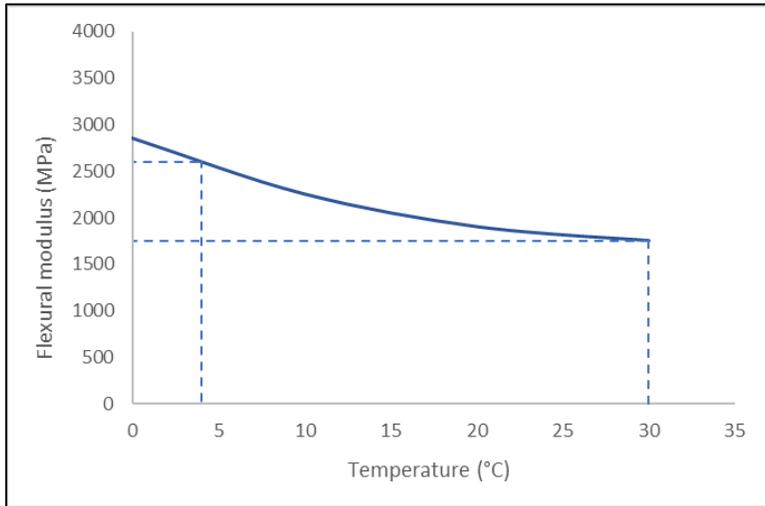
4. Discussion

With the exception of Sustamid® and Sustakon®, the thermoplastic materials absorbed only minor amounts of water and their mechanical properties were largely unaffected by immersion in pressurized artificial seawater for 56 days. Additionally, the epoxy resin/glass fiber composites exhibited relatively low water absorption and good mechanical property retention. This suggests that these thermoplastic and composite materials may be suitable for use in deep ocean equipment. That being said, it is important that designers consider a number of other factors that could impact the performance of polymers in marine applications. Sections 4.1 and 4.2 will highlight some of these considerations.

4.1 The Effect of Temperature

The temperature of the ocean can range from as high as 30 °C at the surface in the tropics to as low as of 4 °C at depths below 200 meters. Thermoplastic materials tend to become stiffer and less ductile at low temperatures. For example, Figure 10 shows that the flexural modulus of propylene homopolymer increases by approximately 50% when the material is cooled from 30 °C down to 4 °C.

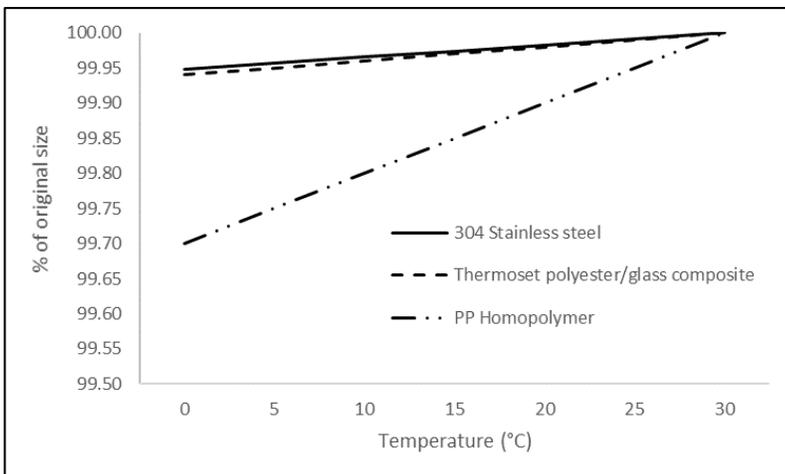
Figure 10. Flexural modulus of homopolymer polypropylene at various temperatures. Adapted from McKeen, 2008 [5].



When offshore equipment includes components made from thermoplastics, composites, and metals, it is important to consider the different thermal expansion/contraction rates of these three families of materials. For example, Figure 11 shows the thermal contraction of polypropylene homopolymer (a semi-crystalline thermoplastic), thermoset polyester/glass composite, and 304 stainless steel when the materials are cooled from 30 °C to 4 °C.

As shown in the figure, stainless steel and polyester/glass composite have similar (low) rates of thermal contraction and polypropylene homopolymer has a higher rate of thermal contraction than the other two materials. The resulting effect on part dimensions must be allowed for when designing mating metal and polymer components for deep ocean applications.

Figure 11. Thermal contraction of 304 stainless steel, thermoset polyester/glass composite, and polypropylene homopolymer.



4.2 The Effect of Hydrostatic Pressure on Dimensions and Mechanical Properties

Machine components will be compressed at high hydrostatic pressures as a function of the bulk moduli of the materials used to manufacture them. Figure 12, adapted from a paper by Regina Middaugh and Clifford Gaudey [7], shows strain as a function of hydrostatic pressure for various materials. In a manner similar to thermal expansion/contraction rates, the bulk moduli of the thermoset composite and the metals are relatively high. The bulk moduli of the thermoplastics (polyamide, HDPE, and PTFE) are relatively low, as indicated by high strain at elevated hydrostatic pressures.

A number of studies have documented the effect of elevated hydrostatic pressure on the mechanical properties of thermoplastics and thermoset composites [3, 6, 8, 9]. The moduli of polymer materials tend to increase with increasing hydrostatic pressure. Figure 13, adapted from a study by K.D. Pae [8], shows the elastic modulus ratio (the ratio of the modulus at elevated hydrostatic pressure to the modulus at atmospheric pressure) for a number of semi-crystalline polymers at various pressures. Hydrostatic pressure equivalent to the pressure in the deepest ocean (1086 bar, 15,750 psi) is indicated on the graph.

Figure 12. Strain as a function of hydrostatic pressure for various materials. Adapted from a paper by Regina Middaugh and Clifford Gaudey [7].

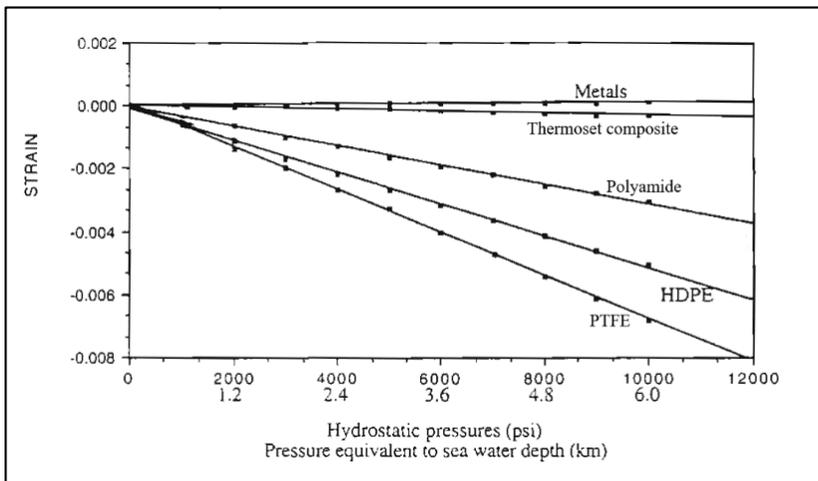
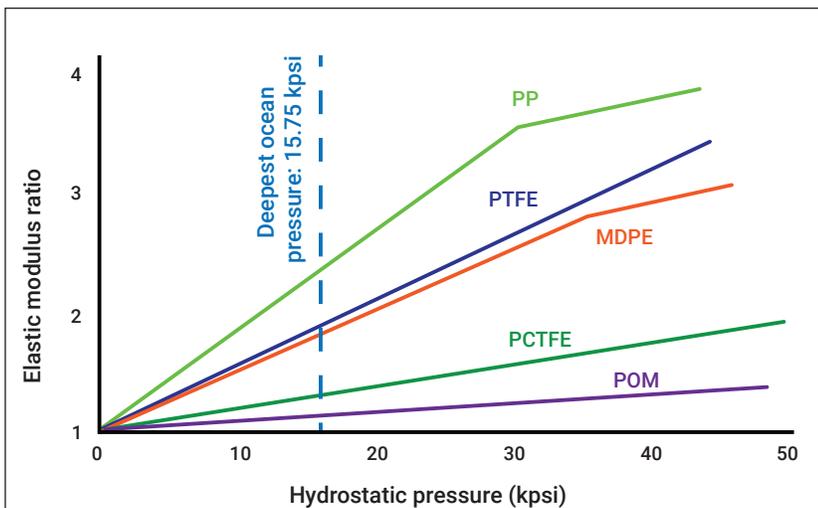


Figure 13. Elastic modulus ratio as a function of hydrostatic pressure for various semi-crystalline polymers. Adapted from a paper by K.D. Pae [8].



4.3 Thermoplastics and Composites with Relatively High Water Absorption

Sustamid® and Sustakon® exhibited higher water absorption and greater reduction of mechanical properties than the other thermoplastics tested. Unsaturated polyester resin composites exhibited higher water absorption than the epoxy composites. That being said, these materials should not necessarily be dismissed as being unsuitable for offshore applications. For example, a number of authors [1, 2, 10] have documented the high water absorption levels and corresponding reduction in mechanical properties for polyamide 6, which is consistent with the results of this study. Figure 14 shows the reduction in flexural stiffness of polyamide 6 when it absorbs water and the increase in stiffness when the material is subsequently dried [2]. Polyamide 6 parts will also increase in size when they absorb water [10].

Although polyamide 6 becomes less stiff and exhibits some swelling when it absorbs water, the material has a number of advantages including low cost, ease of machining, high wear resistance, and the ability to be cast into complex shapes. For these reasons, polyamide 6 is widely used in marine applications even though it has high water absorption. Figure 15 shows ROV thruster nozzles machined from blue cast polyamide 6 tubing.

It is also important to recognize that as a practical matter, polyamide 6 parts with thick wall sections may never experience the full plasticizing effect of water absorption due to the very long exposure time that would be required for the water to diffuse deeply into the core of the part. Additionally, the relatively cold temperatures associated with deep sea applications slow the rate of diffusion, further reducing the plasticizing effect of water absorption in thick walled polyamide 6 parts.

Figure 14. Flexural stiffness of polyamide 6 as a function of water absorption during immersion and then subsequent drying [2]. Source: Francois, Davis, Grosjean, & Legerstee (2010).

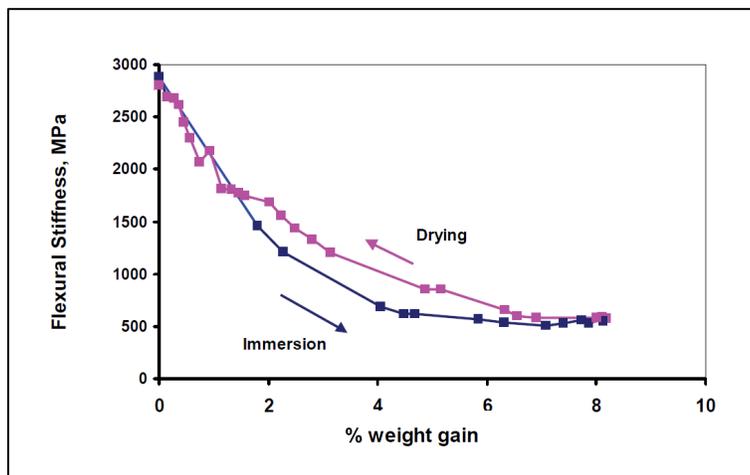


Figure 15. ROV thruster nozzles machined from blue cast polyamide 6 tubing.



This application illustrates that plastics and composites with relatively high water absorption may be suitable for offshore applications either at shallow depths with low hydrostatic pressure or in applications with less demanding load bearing requirements.

5. Conclusions

This study has shown the water absorption characteristics and the corresponding effects on mechanical properties for thermoplastics and composites immersed in seawater at hydrostatic pressure corresponding to an ocean depth of 3500 meters. The results of this research will allow designers of deep ocean equipment to make more informed decisions when specifying polymer materials for offshore equipment.

6. Acknowledgements and Research Notes

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Please note that all findings in this paper are only valid for the mentioned Röchling materials and they can not be generalized to any other materials in the market. The data are provided purely for information and shall not be regarded as binding unless expressly agreed in a contract of sale.

References

- [1] Baschek G., Hartwig G., & Zahradnik F. (1999). Effect of water absorption in polymers at low and high temperatures. *Polymer*, 40, 3433–3441.
- [2] Francois M., Davis P., Grosjean F., & Legerstee F. (2010). Modelling fiber rope load-elongation properties - polyester and other fibers. *Proceedings of 2010 Offshore Technology Conference*, Houston, Texas, 3-6 May, 2010.
- [3] Hoppel, C., Bogetti, T., & Gillespie, J. (1995). Literature review - effects of hydrostatic pressure on the mechanical behavior of composite materials. *Journal of Thermoplastic Composite Materials*, 8, 4, 375-409.
- [4] Le Gac, P, Davies, P. & Choqueuse, D. (2015). Evaluation of long term behaviour of polymers for offshore oil and gas applications. *Oil & Gas Science and Technology*, 70, 2, 279-289.
- [5] Mckeen, L. (2008). *The effect of temperature and other factors on plastics and elastomers*, 2nd edition, 390. Norwich, NY: William Andrew. ISBN: 978-0-8155-1568-5.
- [6] Mears, D., Pae, K., & Sauer, J. (1969). Effects of hydrostatic pressure on the mechanical behavior of polyethylene and polypropylene. *Journal of Applied Physics*, 40, 11, 4229-4237.
- [7] Middaugh, R. & Goudey, C. (1993). The dimensional change of polymers under high hydrostatic pressure. *Proceedings of OCEANS '93*.
- [8] Pae, K. & Bhateja, S. (1975). The effects of hydrostatic pressure on the mechanical behavior of polymers. *Journal of Macromolecular Science, Part C, Polymer Reviews*, 13, 1, 1-75.
- [9] Rhee, K., Leeb, S. & Parkc, S. (2004). Effect of hydrostatic pressure on the mechanical behavior of seawater-absorbed carbon/epoxy composite. *Materials Science and Engineering, A*, 384, 308–313.
- [10] Sepe, M. (2013). Dimensional stability after molding: part 4. *Plastics Technology Online*, March 25th, 2013.

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