

NUWC XP-1 Polyurethane-Urea: A New, “Acoustically Transparent” Encapsulant for Underwater Transducers and Hydrophones

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Abstract - Almost all acoustic projectors and hydrophones are encapsulated in polymeric materials. These coatings protect the underlying sensors and electronics from physical damage and water ingress, while allowing the passage of acoustical energy without significant reflection, loss, or distortion. Critical material parameters for superior acoustical performance include: (1) density and sound speeds close to those of seawater; (2) low mechanical loss tangent; (3) medium to high shear loss tangent; (4) low shear storage modulus; (5) Poisson’s ratio near 0.50; and (6) no major polymeric transitions in/near the frequency and temperature ranges of interest. Recently, a new polyurethane-urea elastomer was synthesized at Naval Undersea Warfare Center (NUWC), Division Newport for use as an encapsulant for transducers and hydrophones. This material, “NUWC XP-1”, utilizes a toluene diisocyanate/polyether polyol base (molecular weight about 1500) and dimethylthiotoluenediamine as the cross-linking/curing agent. NUWC XP-1 cures overnight at room temperature to 75 Shore A hardness. Its sound speed is very close to that of seawater at room temperature, and at 25°C, its acoustic impedance is 1.71×10^6 metric Rayls. NUWC XP-1 exhibits a sub-ambient glass transition temperature (-31°C) and its dynamic mechanical properties are almost ideal for underwater transducer/hydrophone encapsulants. Side-by-side comparisons with several commonly used, commercially-manufactured polyurethane encapsulants (PRC-DeSoto’s PR-1547 and PR-1592; Cytec’s Conathane EN-7) determined that properties of NUWC XP-1 are equal to, or better in almost every category required for effectively encapsulating acoustic devices and sensors. A distinct benefit to the industry is that the chemical formula of NUWC XP-1 is controlled by the U.S. Navy. The material is made from basic raw materials; thus its future availability is more assured than many other commercial products.

I. INTRODUCTION AND BACKGROUND

Polyurethane elastomers have been used to encapsulate U.S. Navy acoustic projectors and hydrophones since the 1970s. Polyurethanes exhibit a number of desirable properties that have lead to their widespread use as encapsulants: (1) close density and sound speed matches with seawater (determines characteristic acoustic impedance); (2) Poisson’s ratios near 0.50; (3) low shear storage modulus and high shear loss tangent; (4) moderately low water absorption and water permeability; and (5) ease of use/ability to cure at room temperature. Over the past 20 years, a number of commercial off-the-shelf (COTS) polyurethanes from a variety of different manufacturers have been used as encapsulants by Navy laboratories and Navy contractors. While these COTS polyurethanes have performed adequately over the years, many of the materials were not specifically designed for encapsulating acoustic devices. Hence, their acoustic performance, while “adequate” in most cases, could be improved. Another problem that has been encountered with COTS materials is that, in most cases, their actual chemical formula and structure are proprietary, and hence unknown. Manufacturers have changed chemical formulas without informing end users. Frequently, some of the materials’ desirable acoustic properties have been adversely affected by such changes in formulation. In other instances, the manufacture of specific products has been terminated altogether for reasons beyond the control of the Navy. Product terminations and formula changes have rendered meaningless large amounts of acoustic data collected over the years on the affected materials, and have forced the unplanned expenditure of significant funds to find and characterize suitable replacement materials.

Clearly, it is advantageous for the Navy to develop from scratch one or more polyurethane-based acoustic encapsulants. The chemical formula for such materials would be in the public domain, and anyone could make them from the basic raw materials specified by the formulas. This would eliminate the possibility of a “secret” formulation change, and it would also ensure product availability, because only

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basic, raw chemical components would be needed to produce the resins. The expense of a full acoustic characterization is easy to justify because the likelihood of the material becoming unobtainable for any reason would be remote.

About two years ago, the Underwater Sound Reference Division (USRD) at the Naval Undersea Warfare Center, Division Newport (NUWC DIVNPT), asked the polymer chemists in NUWC DIVNPT's Transducer Materials Branch to re-initiate the formulation of a polyurethane compound potentially used to encapsulate some transducer Standards. This particular polyurethane had been partially developed at the Naval Research Laboratory's (NRL) Underwater Sound Reference Detachment in Orlando, Florida and exhibited a very close sound speed match with seawater at room temperature. The chemical structure of this particular polyurethane suggested that it should perform well as a transducer encapsulant [1], [2].

II. CHEMISTRY AND PHYSICAL PROPERTIES

During calendar year 2002, the NRL-Orlando polyurethane formulation was revived at NUWC DIVNPT. The resulting material was christened "NUWC XP-1 Polyurethane." NUWC XP-1 is a two part polyurethane-urea elastomer that can be cured at room temperature or elevated temperatures. The "resin" component is a blend of two Voranol™ (Dow Chemical Company) polyether polyols designed to have a molecular weight average of 1500 grams/mole. This blend is achieved by mixing polyether polyols with molecular weights of 1000 and 200 grams/mole together. The resulting mixture is then reacted with a slight excess of toluene diisocyanate (TDI; a mixture of 80% toluene 2,4-diisocyanate and 20% toluene 2,6-diisocyanate) at 70°C for 16 hours. The resulting prepolymer resin is clear and of moderate viscosity. Under a nitrogen purge, the NUWC XP-1 prepolymer resin ("Part A") has a storage life of at least one year at room temperature. The curing agent for NUWC XP-1 is dimethylthiotoluenediamine (DMTDA). This chemical is available commercially from the Albemarle Chemical Corporation as "Ethacure 300." The recommended mixing ratio of prepolymer to curing agent is 100 to 11.5 parts by weight. NUWC XP-1 will cure overnight at room temperature. Curing can be accelerated by heating the material in an oven. Because the polymerization (curing) reaction involves a reaction between an isocyanate group on a prepolymer molecule and an amine group on a curing agent molecule, the major chemical change during curing is the formation of urea linkages. Thus, NUWC XP-1 is technically classified as a polyurethane-urea elastomer, rather than a polyurethane, but for the purposes of this paper, it will be referred to as a polyurethane.

Fully cured NUWC XP-1 polyurethane is a flexible, clear elastomer with a faint amber tinge. The curing agent, dimethylthiotoluenediamine, darkens over time upon exposure to oxygen. Thus, samples of NUWC XP-1 made with fresh curing agent are transparent with only a hint of an amber hue, but samples made with aged or improperly sealed

curing agent appears darker in appearance. The Shore A hardness of NUWC XP-1 is 70 ± 5 Shore A units. The density of cured NUWC XP-1 is 1090 kg/m^3 .

As the temperature is lowered, most "soft" elastomeric materials like NUWC XP-1 polyurethane will become much stiffer and brittle. The temperature at which the material changes from being soft and flexible to hard and brittle (and vice-versa) is called the "glass transition" temperature, and it is an important property for such polymers. Passage through the glass transition triggers a large change in modulus. From an acoustic perspective, it is important to know the glass transition temperature for an elastomeric encapsulant, because the temperature region in which it occurs tends to be very lossy in a mechanical sense. Because the mechanical loss tangent ($\tan \delta$) is high in and around the glass transition temperature, it is very desirable that the glass transition temperature be as low as possible. The glass transition temperature of NUWC XP-1 polyurethane, measured by dynamic mechanical analysis at 1.0 Hz and a heating ramp of 2.5°C/minute, is -31°C. This temperature is well below the lowest operating temperatures for sonar systems (0+°C), and it compares favorably with similar measurements made on other polyurethanes used as encapsulants (e.g., PR-1592 at -2°C; PR-1547 at -16°C; and Conathane EN-7 at -54°C).

The tensile strength (ASTM D-412) of NUWC XP-1 polyurethane is about 1600 psi. This is lower than the comparable values for PR-1592, PR-1547, and Conathane EN-7 polyurethanes. On the other hand, both the ultimate elongation (ASTM D-412) of 900%, and tear strength (ASTM D-624) of 400 pli exhibited by NUWC XP-1 polyurethane are considerably higher than the corresponding values for the other three polyurethane encapsulants.

All polyurethanes will absorb some water when submerged in a marine environment. Polyether-based polyurethanes absorb less water over time than polyester-based polyurethanes (the other major class of polyurethanes) and, in addition, they are not as susceptible to hydrolysis. The polymer backbone of NUWC XP-1 polyurethane is polyether-based; thus, it is expected to resist water absorption. In the Navy materials community, there is no consensus or formal guidance as to what the maximum allowable amount of water absorption by a polyurethane encapsulant should be because applications are generally unpredictable. There are some values in the literature for rubber-based encapsulants, but the testing protocols are not the same. Ting [3] recommended a maximum allowable weight change of +1.4% after soaking in seawater for 48 hours at room temperature. Thompson and Buemel [4] recommended a maximum allowable weight change of +3.0% after soaking in seawater for 14 days at 55°C. When samples of NUWC XP-1 were tested in accordance with the procedures specified in those two documents, the results were +0.5% (for Ting's method) and +2.0% (for Thompson and Buemel's method). Thus, NUWC XP-1 polyurethane exhibits acceptable water absorption characteristics.

III. ACOUSTIC PROPERTIES

The acoustic properties of NUWC XP-1 polyurethane are of greatest interest to transducer designers. These properties will determine how well the material would be expected to perform as an encapsulant or in an acoustic window application.

Two very important acoustic properties are sound speed within the material and its acoustic impedance (acoustic impedance is defined as density multiplied by sound speed). At NUWCDIVNPT, polymer sound speed measurements are made using a pulse-echo time-of-flight system that utilizes a transducer operating at 2.25 MHz. The frequency of the transducer is significantly higher than the frequencies of interest in Navy sonar systems. Because sound speed is a function of modulus, and modulus is a function of frequency, the sound speeds measured using 2.25 MHz are undoubtedly higher than they would be for more realistic sonar frequencies (e.g., less than 100 kHz). However, the system is useful as a screening tool, because the size of the sample is quite small, and the measurements can be made easily and rapidly. Using this system, the speed of sound in NUWC XP-1 polyurethane was measured to be 1570 m/sec at room temperature. At this temperature, the speed of sound in seawater is about 1500 m/sec. Thus, the sound speed match between seawater and NUWC XP-1 polyurethane is quite good. Using this sound speed and the density of NUWC XP-1 at room temperature, the material's acoustic impedance is 1.71×10^6 metric Rayls. The match with seawater is within 12% (the acoustic impedance of seawater is 1.53×10^6 metric Rayls at room temperature). Because of the close acoustic impedance match between NUWC XP-1 and seawater, and because the value of Poisson's ratio for NUWC XP-1 is close to 0.50, the amount of incoming acoustic energy that is reflected from the seawater/XP-1 interface is minimal.

There are several additional considerations for the acoustic performance of a polymeric encapsulant. First, the mechanical loss tangent ($\tan \delta$) should be as low as possible throughout the temperature and frequency ranges of interest. This requirement minimizes the amount of acoustic energy that is converted into heat (random molecular motions) and therefore lost, as the acoustic energy transits through the polymer. In addition, the shear storage modulus should be as low as possible, and the shear loss tangent ($\tan \delta$) should be as high as possible throughout the temperature and frequency ranges of interest. These requirements are intended to minimize the amount of energy converted from longitudinal (sound) waves into shear waves within the polymer. A low shear storage modulus minimizes the amount of energy converted into shear waves, and a high shear loss tangent helps to dissipate any shear waves that are generated (so that they do not combine destructively at the sensor or at a subsequent water/polymer interface). All of these properties can be measured in a straightforward manner by dynamic mechanical analysis (DMA) at relatively low frequencies. Once the data has been collected for several frequencies over a wide temperature range, material performance can be

predicted for higher (and lower) frequencies through the use of time-temperature superposition principles. Processing data originally collected by DMA in this manner allows the construction of plots of moduli and loss tangents that would be impossible to obtain via direct measurement using the same equipment.

Time-temperature superposition generated plots of several different mechanical properties versus temperature at fixed frequencies of interest have been generated for NUWC XP-1 polyurethane. At 10 kHz, the mechanical loss tangent ($\tan \delta$) falls from about 0.35 at 0°C to less than 0.20 above 20°C. These values are comparable to and, at some temperatures, lower than, the corresponding values for other polyurethane encapsulants. A plot of shear loss modulus ($\tan \delta$) versus temperature at 10 kHz indicate that the material exhibits a relatively high shear loss tangent (0.25 to 0.20) between 0°C and 40°. Finally, the shear modulus of NUWC XP-1 is relatively low (100 to 150 MPa) compared to other polyurethane encapsulants from about 15°C to 40°C, though it increases to about 275 MPa as the temperature drops from 15°C to 0°C. These results indicate that NUWC XP-1 should perform as good as and, in many cases, better than the polyurethanes presently being used as transducer and hydrophone encapsulants [5] – [7].

Recently, a series of acoustic tests were conducted on a large (30 inch by 30 inch by 1 inch) panel in an acoustic pressure test facility (APTF) at NUWCDIVNPT. This testing allowed the longitudinal sound speed, shear sound speed, insertion loss and attenuation of NUWC XP-1 polyurethane to be directly measured at typical sonar frequencies (between 10 and 100 kHz) [8]. The longitudinal sound speed varied from about 1640 m/sec at 3°C and 100 kHz, to about 1400 m/sec at 35°C and 10 kHz. At 20°C, the longitudinal sound speed in NUWC XP-1 polyurethane was very close to the speed of sound in seawater at the same temperature (about 1460 m/sec). The measured shear sound speeds in NUWC XP-1 polyurethane were uniformly low (approximately 1/5 of the corresponding longitudinal sound speed for the same frequency and temperature). The insertion loss for the one-inch thick panel was highest at the lowest test temperature (3°C) and decreased as the temperature increased. At constant temperature, insertion loss increased as frequency increased. For example, at 3°C, the insertion loss varied from about 0.2 dB at 10 kHz to about 3 dB at 100kHz; but at 35°C, the insertion loss varied from about 0 dB at 10 kHz to about 1 dB at 100 kHz. Finally, the attenuation within the panel was uniformly low (never exceeding 0.14 nepers/cm even at 3°C and 10 kHz). Attenuation increased linearly with frequency at fixed temperature.

IV CONCLUSIONS:

The acoustic, physical, and chemical properties of NUWC XP-1 polyurethane provide for a practical encapsulant for underwater acoustic devices. The material was designed to match the acoustic properties of seawater at room

temperature as closely as possible, and the experimental data collected to date indicates that this goal has been achieved. In addition, NUWC XP-1 exhibits mechanical loss tangent, shear loss tangent, shear storage modulus, acoustic attenuation, and insertion loss values that are consistent with its intended end-use as a transducer/hydrophone encapsulant. The material is synthesized from basic raw materials whose widespread availability and known chemical structures should ensure that NUWC XP-1 can be produced in quantities necessary to meet the demand for the foreseeable future. NUWC XP-1 polyurethane has been characterized acoustically and, even though it has limited time out in the field, has every indication that it will perform very well in its intended role as an encapsulant for underwater acoustic sensors and projectors.

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