

Development of Seawater-Resistant Polyurethane Elastomers for Use as Sonar Encapsulants

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SYNOPSIS

Polyurethane systems based on aliphatic diisocyanates were evaluated for suitability for use as underwater transducer encapsulants. A preliminary evaluation was performed to select the most promising urethane systems for further development. An investigation was then undertaken to determine the effect of compositional changes on the properties of these urethanes. The compositional parameters investigated were the soft-segment molecular weight, the prepolymer isocyanate content, the composition of the cure formulation, and the cure stoichiometry. These urethanes were subjected to long-term aging in seawater. It was found that this exposure did not significantly effect the physical or dynamic mechanical properties of the urethane.

INTRODUCTION

A wide variety of elastomers including butyl rubber, neoprene, and polyurethanes are used in the fabrication of underwater sonar devices.¹⁻³ These elastomeric materials are used to encapsulate the surface of a ceramic transducer and must possess specific acoustic properties to ensure minimal interference with the transducer's acoustic performance. These special requirements are in addition to the need for good mechanical properties and ease of handling. It is also necessary that the encapsulant material have a low water permeation constant to protect the transducer from the ingress of seawater and be able to withstand prolonged exposure to seawater without significant deterioration of its properties. Due to this rather stringent set of requirements, polyurethanes have been given considerable attention as potential encapsulant materials. Polyurethanes have the potential for greater property variations caused by changes in composition of the component base materials. In contrast, property variations in rubbers are mainly achieved by changes in compounding. In addition, polyurethanes offer greater ease of fabri-

cation since they are typically obtained from castable liquid components. Polyurethanes that have been used as underwater encapsulants typically have been optimized for other applications. Therefore, a research effort was undertaken to develop nonproprietary polyurethane formulations for underwater transducer encapsulants. Since the specific acoustic requirements will depend on the function of the particular transducer, it is not possible to specify one optimum formulation for an encapsulant. It is therefore necessary to determine how the properties of a particular polyurethane system can be altered by suitable changes in its formulation. The systems considered were based on aliphatic diisocyanates, which are less reactive than conventional aromatic isocyanates. These aliphatic systems should have longer pot lives and improved handling characteristics. It was also believed that these aliphatic isocyanates would yield urethanes with improved hydrolytic stability.⁴

ACOUSTIC BACKGROUND

Sonar transducers operate over a wide range of temperature, pressure, and sound frequency. It is desirable that these elastomeric encapsulants exhibit low loss in shear or extension over the temperature and

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frequency range of a transducer's operation. In addition, it is important that the encapsulant have a density and dilatational wave velocity that give a close acoustic impedance match to seawater at normal incidence. The average specific acoustic impedance of seawater is $1.6 \times 10^6 \text{ kg/m}^2 \text{ s}$ (rayl), although it will vary with factors such as depth, ocean temperature, and salinity.⁵ The specific acoustic impedance is defined as the product of the material's density and longitudinal velocity or sound speed. The densities of commercial urethanes are typically in the range of $1.0\text{--}1.5 \text{ g/cm}^3$.⁶ Therefore, to obtain a close impedance match to seawater it is necessary that the speed of sound through the urethane be in the range from 1450 to 1550 m/s. There have been only a few published studies on the sound speed of polyurethanes and most of these were made on commercial compounds with proprietary compositions.⁵⁻⁷ One study did investigate the effect of composition on the sound speed of a urethane.⁶ The authors found that significant reductions in the sound speed could be obtained by increasing the average molecular weight or the relative amount of the soft block of the urethane. The amount of soft block was increased most easily by adding high molecular weight polyols to the cure formulation. This method allows one to obtain a urethane with lower sound speed from a commercial prepolymer without having to change the composition of the prepolymer itself.

The requirement that an encapsulant material have a low loss in shear or extension is difficult to satisfy due to the wide range of temperature and frequency over which a transducer may operate. The soft block component of most urethanes undergoes its glass transition at temperatures in the range from -50 to -100°C . This transition causes the urethane to have a large loss tangent in this temperature range in low-frequency dynamic mechanical experiments. As the frequency increases, this low-temperature loss peak will broaden and shift to higher temperatures as described by the time-temperature superposition principle.⁸ Sonar transducers operate over a wide frequency range that may extend above 100 kHz.⁵ At these high frequencies the high loss tangent associated with the soft segment glass transition will begin to be observed at temperatures that are in the range of operation of the transducer. To minimize the effect of this soft block glass transition, it is desirable to employ urethanes based on soft block components having fairly low glass transition temperatures. Therefore, polytetramethylene glycol (PTMEG), which has glass transition near -70°C , is preferred as the polyether soft block component over a polyether such as polypropylene glycol, which

has a higher glass transition near -50°C .⁹ However, the glass transition associated with a PTMEG soft segment will have some effect at the higher operational frequencies. It is therefore desirable to attempt to minimize the magnitude and sharpness of the loss tangent as a function of frequency in the glass transition region, by modification of the polyurethane's composition.

EXPERIMENTAL

Polyurethane prepolymers were obtained from Anderson Development Company, Polyurethane Corporation of America, and American Cyanamid Company. Additional prepolymers were synthesized by reacting an excess of the diisocyanate with polytetramethylene glycol as described previously.⁴ A small amount, 0.01–0.04%, of a metal catalyst, ferric acetylacetonate, was added to each of the cure formulations used. The prepolymer and cure formulation were preheated to 70°C and degassed prior to mixing. To form a cured polyurethane the prepolymer and curative were mixed thoroughly, degassed again and poured into a preheated mold. Once in the mold, the sample was degassed briefly to eliminate any remaining voids. The polyurethane was allowed to cure at 70°C for 18 h, demolded, and postcured at ambient conditions for at least 2 weeks.

The hardness was measured at 25°C with a constant-rate, constant-load Shore A durometer after 15 s. The densities were obtained at 25°C by the Archimedes principle. Sound speeds were measured in a Mapco Corporation sonic solution monitor by a method similar to that of Zacharias et al.¹⁰ In this method the time of flight of a 1.5-MHz sound pulse is measured at 25°C both for water and for the sample in water. The sound speed of the sample is then calculated from these time readings. The tensile measurements were made on an Instron tensile tester with a crosshead speed of 500 mm/min. In seawater absorption studies the samples were removed from the seawater at regular intervals, surface dried briefly with a kim wipe, weighed on a Mettler analytical balance, and immediately reimmersed in seawater.

Dynamic mechanical properties were measured by means of a resonance method developed at our laboratory.¹¹ The principle of the measurement is based on measuring the transmissibility of a mass-loaded rod with high internal damping undergoing longitudinal sinusoidal excitation. The sample is harmonically excited using discrete frequency excitation. By solving the equations of motion within

the sample, Young's modulus and the loss tangent are obtained. The seed values obtained at resonance may also be used to solve the equation of motion at frequencies other than resonance. This dynamic data is extrapolated to higher frequencies using a time-temperature superposition principle. Lower temperature dynamic mechanical data were obtained on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) at frequencies from 1 to 30 Hz. The sample chamber was cooled to -80°C using a liquid nitrogen cryogenic cooler, and data was taken while the sample was being heated at a rate of $2^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Preliminary Screening

Several commercial polyurethane prepolymers were obtained for preliminary evaluation. The initial screening was based on being able to obtain a close sound speed match to seawater. These prepolymers were all cured with the liquid diamine, diethyltoluene diamine (DETDA), as the sole component in the cure formulation. The measured sound speeds obtained for the resultant urethanes are listed in Table I, along with their densities and Shore A hardness values. It is clear from these results that all of the urethanes based on the meta and para isomers of

tetramethyl xylene diisocyanate have sound speeds close to that of seawater. All of the other prepolymers formed urethanes having significantly higher sound speeds. Attempts were made to obtain urethanes with lower sound speeds from these prepolymers by addition of polyols into the diamine cure system. These efforts were concentrated mainly on the Andur 80 prepolymer, which had yielded the urethane with the lowest sound speed other than the tetramethyl xylene diisocyanate based prepolymers. The results of these experiments are summarized in Figure 1. In this figure the urethane's sound speed is plotted as a function of the percent of amine in the cure formulation. It is clear that some lowering of the sound speed was achieved by incorporation of polyols into the cure formulation. However, even in the extreme case of a cure formulation containing only 20 mol % of diamine, the Andur 80 prepolymer formed a polyurethane with a sound speed greater than 1600 m/s. Use of a cure formulation containing only polyols resulted in the formation of a urethane that had very poor mechanical properties. On the basis of these results it was decided the American Cyanamid prepolymers were the most promising for use as underwater encapsulants, and the remaining work was done evaluating these systems.

Cured samples of the four tetramethyl xylene diisocyanate based urethanes were immersed in seawater for 8 weeks at temperatures of 25, 55, and

Table I Properties of Several Polyurethanes Obtained from Commercial Prepolymers

Prepolymer	Sound Speed (m/s)	Hardness Shore A	Density (g/cm ³)
Andur 80 ^a	1706	90	1.05
Andur 95 ^a	1825	< 95	1.06
PCA 4-2 ^b	1673	68	1.05
American Cyanamid [PPG TMXDI (META) aliphatic isocyanate] ^c	1555	76	1.06
American Cyanamide [PTMG TMXDI (META) aliphatic isocyanate]	1587	73	1.04
American Cyanamide [PPG TMXDI (PARA) aliphatic isocyanate]	1505	72	1.06
American Cyanamide [PTMG TMXDI (PARA) aliphatic isocyanate]	1579	70	1.05

^a Product of Anderson Development Company.

^b Product of Polyurethane Corporation of America.

^c Trademark of American Cyanamid Company.

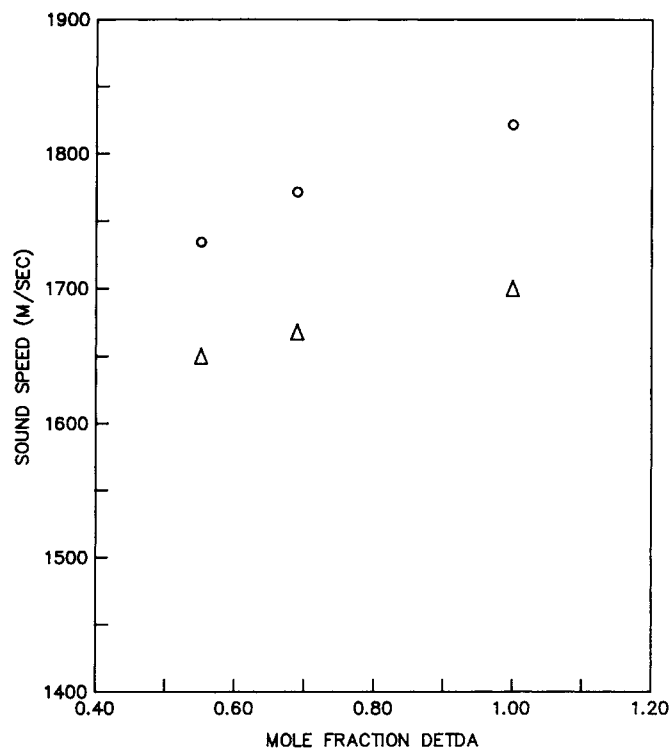


Figure 1 Plot of the sound speed as a function of diamine curative content for the urethanes obtained from the prepolymers: Δ Andur 80, \circ Andur 95.

70°C. The samples were periodically removed and weighed during the 8-week exposure period. The results of this study are summarized in Table II in which the final weight gain of these samples at each of the temperatures is given. There was no discernible difference in the amount of weight gained by the urethanes obtained from the meta and para isomers. The PPG-based urethanes did gain slightly more weight than the PTMEG urethanes. However, the important fact is that none of the samples gained a significant amount of weight even at the highest temperature of 70°C. In a study of polyurethanes

based on the aromatic diisocyanate, toluene diisocyanate, it was found that immersion at 70°C resulted in slightly larger weight gains that ranged from 2.0 to 2.5%.¹² These results strongly suggest that these tetramethyl xylene diisocyanate based urethane systems should have good seawater resistance. At this point, it was decided to concentrate the more detailed studies on the urethane systems containing the meta isomer of tetramethyl xylene diisocyanate. This decision was based on the fact that the meta isomer would soon be commercially available while the availability of the para isomer was uncertain. As discussed earlier, polyurethanes based on PTMEG are more desirable as transducer encapsulants than PPG urethanes due to the lower glass transition temperature of the PTMEG polyether. However, PPG-based prepolymers do have the advantage of lower viscosity resulting in greater ease of handling and processing. Therefore, although more work was concentrated on the PTMEG urethanes, some further testing was done on the PPG systems for possible applications where low dynamic loss was not of primary concern.

Compositional Studies

Having identified the most promising urethane systems, work was begun to investigate the effect of compositional changes on the properties of these urethanes. The compositional parameters investigated were their soft segment molecular weight, the prepolymer isocyanate content, the cure formulation, and the cure stoichiometry. The initial results reported here were done with prepolymers having PTMEG and PPG molecular weights of 2000 g/mol. To investigate the effect of soft segment molecular weight, two prepolymers were synthesized using 1000 molecular weight PPG and PTMEG. Due to the lower soft segment molecular weight, these prepolymers had available isocyanate contents of nearly

Table II Seawater Absorption of Polyurethanes Obtained from the Meta and Para Isomers of Tetramethyl Xylene Diisocyanate Based on Prepolymers Cured with DETDA

Time (h)	Temperature (°C)	Percent Weight Gain			
		Meta Isomer		Para Isomer	
		PTMG Based	PPG Based	PTMG Based	PPG Based
1370	25	1.0	1.8	1.0	1.6
1060	55	1.4	1.9	1.1	2.0
1056	70	1.6	1.9	1.1	2.4

8%. The prepolymers were cured with 100 PPH of DETDA and the sound speeds of the resultant urethanes were measured. Both of the urethanes were found to have sound speeds in excess of 1700 m/s. It was concluded that using these lower molecular weight polyethers would not yield urethanes suitable for use as underwater encapsulants. Since higher molecular weight PTMEG segments are likely to crystallize,⁹ it was decided that a molecular weight near 2000 g/mol would yield the best urethanes for encapsulation applications.

The second compositional parameter to be investigated was the composition of the curative used. Diamine curatives are typically more reactive but yield urethanes with better mechanical properties than dialcohol curatives.¹³ Since adequate pot lives and good acoustic properties were obtained with a pure diamine curative, no effort was made to incorporate polyols into the cure formulation. However, it was felt that improved seawater resistance and mechanical properties might be obtained if a trifunctional curative was added to the formulation. Therefore a PTMEG-based prepolymer was cured with a series of formulations in which varying amounts of the triamine, 2,4-bis(*p*-aminobenzyl) aniline (BABA), was added to DETDA. The mechanical properties of the resultant urethanes are listed in Table III along with the properties measured after 2-week exposure to 85°C and 100% rel-

ative humidity. It is clear from Table III that the incorporation of BABA into the cure formulation results in the formation of polyurethanes with poorer mechanical properties. It appears that the trifunctional curative may give some improvement in resistance to moisture exposure, but any improvement is not enough to compensate for the reduction in the properties of the unaged urethanes. As a result, the urethanes obtained from the BABA-rich cure formulations have poorer properties after the high-temperature exposure to 100% relative humidity. On the basis of these results it was determined that a cure system containing DETDA as the sole component (along with a small amount of catalyst) would be more desirable.

To investigate the effect of prepolymer isocyanate content on the resultant polyurethanes, several PTMEG-based prepolymers were synthesized containing varying amounts of the meta isomer of tetramethyl xylene diisocyanate. These prepolymers were cured with DETDA and the properties of the cured urethanes were measured. The results of these measurements are summarized in Table IV. It is clear from Table IV that an increase in isocyanate content causes a slight increase in the sound speed of the resultant urethane. However, for most acoustic applications, all of these urethanes have an acceptable specific acoustic impedance match to seawater. The longitudinal bulk modulus, M' , was cal-

Table III Hydrolitic Stability of Five Different Polyurethanes Obtained from a Prepolymer Based on PTMEG and Meta Tetramethyl Xylene Diisocyanate

Cure Composition					
Mole fraction DETDA	100	90	80	70	60
Mole fraction BABA	0	10	20	30	40
Physical Properties (initial)					
Hardness	85A	81A	81A	82A	80A
100% Modulus (MPa)	5.04	5.26	3.97	5.43	5.38
Tensile strength (MPa)	35.0	28.4	29.0	26.6	19.8
Elongation (%)	493	461	432	393	328
Physical Properties (after aging)					
Hardness	76A	76A	74A	73A	72A
100 % Modulus (MPa)	3.05	3.46	3.32	3.35	3.19
Tensile strength (MPa)	16.4	13.7	13.0	13.4	13.1
Elongation (%)	739	698	656	566	469

Table IV Properties of Polyurethanes with Various Amounts of the Meta Tetramethyl Xylene Diisocyanate Group

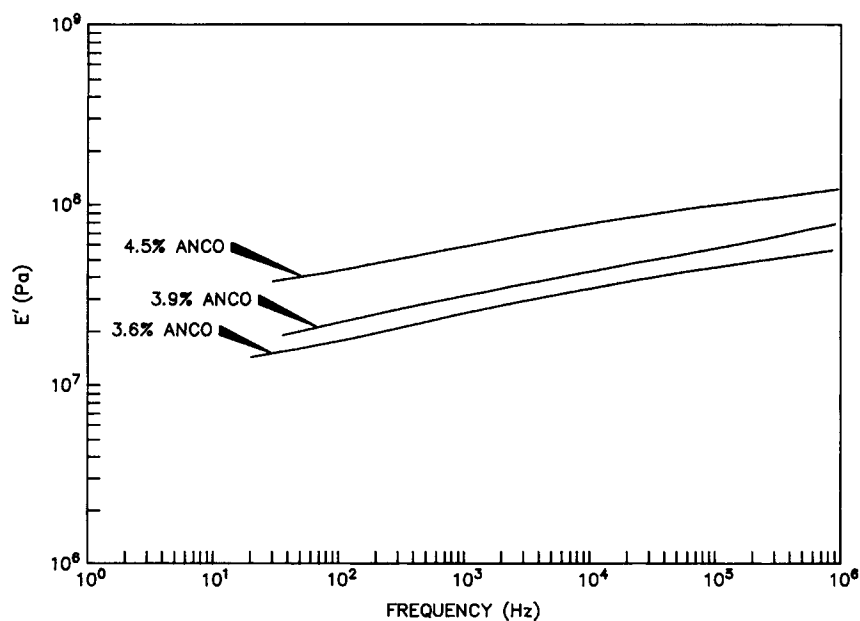
Isocyanate Content	Hardness Shore A	Density (kg/m ³)	Sound Speed (m/s)	Acoustic Impedance (rayl)	Deviation from Seawater (%)	300% Modulus (MPa)	M' (Pa)
3.6	63	1.03×10^3	1579	1.63×10^6	1.79	3.6	2.57×10^9
3.9	68	1.03×10^3	1583	1.63×10^6	2.13	4.2	2.58×10^9
4.5	75	1.04×10^3	1604	1.67×10^6	3.79	6.4	2.68×10^9

culated from the product of the density and the square of the sound speed. These results correspond to the value of M' at 1.5 MHz, which is the frequency at which the sound speed measurements were made. The increase in isocyanate content causes some increase in the value of the longitudinal bulk modulus.

The variation in isocyanate content does cause a more significant change in Shore A hardness, but all of the urethanes have acceptable hardness values. The results of the tensile testing also shown in Table IV indicate that the variation in isocyanate content does have a significant effect on the modulus of the urethane. The values of tensile strength and ultimate elongation are not reported because most of the samples did not break at the maximum elongation of the Instron. However, these tensile tests indicate that a tensile strength of 14.2 MPa and an ultimate

elongation of 650% are lower limits to the actual values for these urethanes.

In addition, each of these prepolymers were cured into samples suitable for dynamic mechanical testing. The results obtained by the previously described resonance method are summarized in Figures 2-4. In Figure 2 the dynamic Young's moduli of these polyurethanes are plotted as a function of frequency for a reference temperature of 25°C. It is clear that the modulus increases with increasing isocyanate content consistent with the tensile results listed in Table IV. These results are also consistent with the increase in Shore A hardness caused by the reinforcing effect of higher hard segment content. The static Young's moduli, as estimated from the hardness measurements, were 4, 5, and 8×10^6 Pa. The observed increase in the longitudinal bulk modulus

**Figure 2** Plot of the dynamic Young's modulus as a function of frequency measured at 0°C for the polyurethanes with the indicated isocyanate contents.

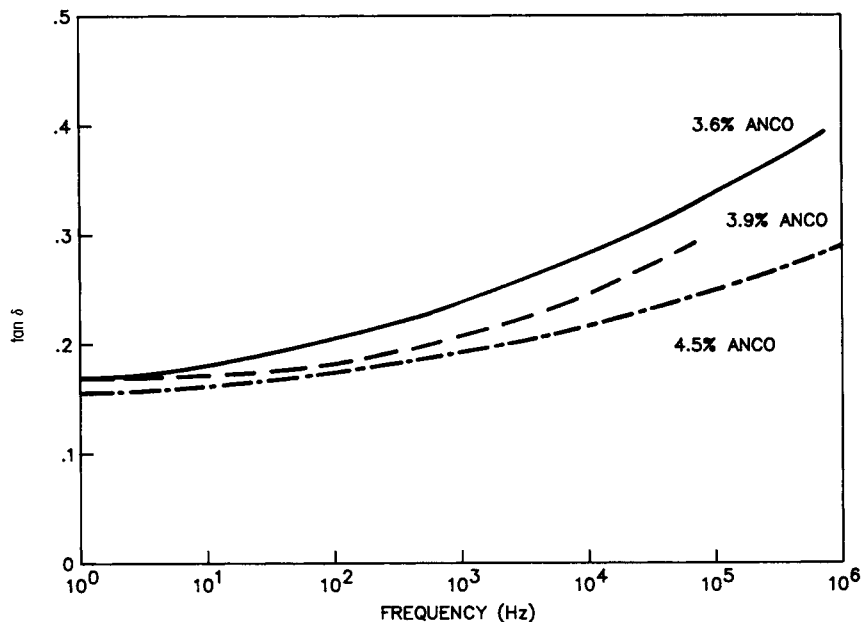


Figure 3 Plot of the loss tangent as a function of frequency measured at 0°C for the polyurethanes with the indicated isocyanate contents.

can also be explained by this increase in the high-frequency Young's modulus with increasing isocyanate content. The longitudinal bulk modulus has both a bulk and shear modulus component. The results shown in Figure 2 suggest that the shear or Young's modulus component of the longitudinal

bulk modulus causes the observed increase with isocyanate content.

Of greater interest for encapsulant applications is the behavior of the loss tangent of these urethanes at high frequency. In Figures 3 and 4 the $\tan \delta$ curves for each of these urethanes are plotted as a function

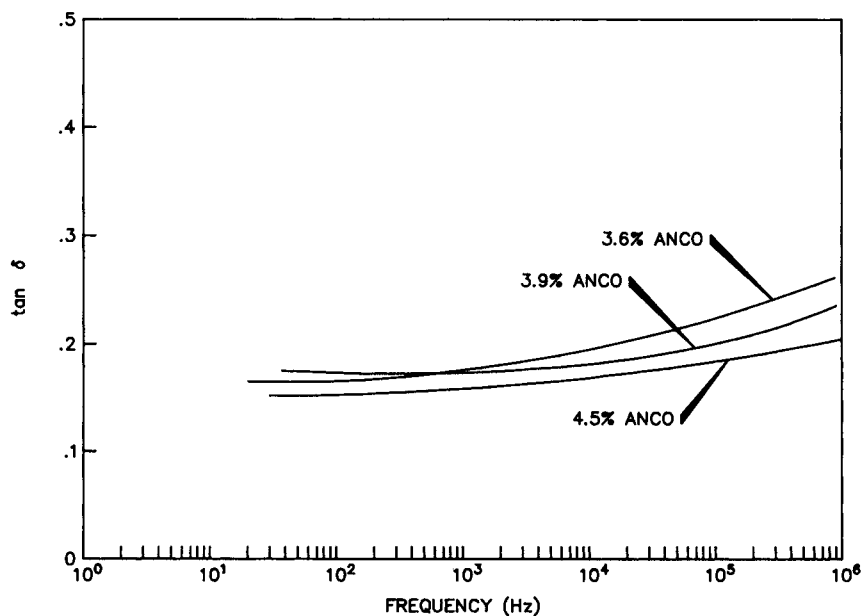


Figure 4 Plot of the loss tangent as a function of frequency measured at 25°C for the polyurethanes with the indicated isocyanate contents.

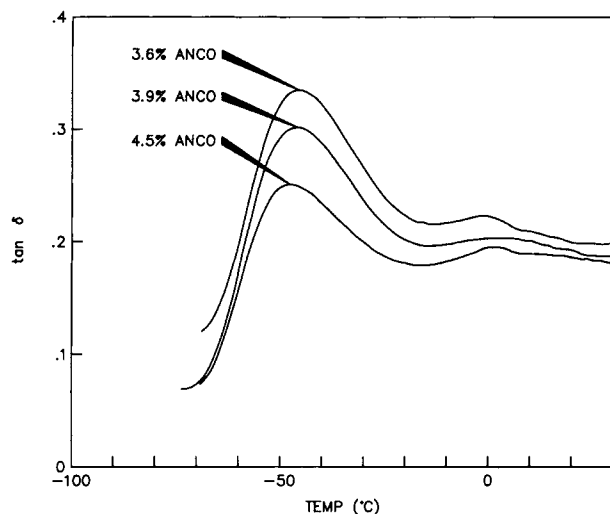


Figure 5 Plot of the loss tangent as a function of temperature measured at 10 Hz for the polyurethanes with the indicated isocyanate contents.

of frequency at reference temperatures of 0 and 25°C. The increase in $\tan \delta$ at high frequencies is due to the onset of the glass transition of the PTMEG soft segment. At a temperature of 0°C the urethane obtained from the 3.6% prepolymer has its loss tangent increase to a value of 0.3 at a frequency near 10^4 Hz. The 3.9% urethane has a slightly lower loss tangent over this frequency range and does not reach a loss tangent of 0.3 until the frequency is increased to almost 10^5 Hz. The 4.5% urethane follows the same trend and has even lower $\tan \delta$ values over this frequency range. At the higher temperature of 25°C a low loss tangent is obtained over an even wider frequency range. At this higher temperature, it is necessary to go to higher frequencies to approach the onset of the PTMEG glass transition. These results indicate that the prepolymer isocyanate content should be kept at a value greater than 4% to obtain a polyurethane with low dynamic loss over a wide-frequency range and good mechanical properties. However, if a very close specific acoustic

impedance match to seawater is required, a lower isocyanate content could be used.

Low-frequency dynamic mechanical measurements were also made on these urethanes over a wide temperature range on a dynamic mechanical thermal analyzer (DMTA). The measured $\tan \delta$ values for these urethanes are plotted as a function of temperature in Figure 5. Since these measurements are begun at low temperatures, the entire $\tan \delta$ peak associated with the glass transition of the PTMEG portion of these urethanes can be observed. The results shown in this figure confirm the previous conclusion that the magnitude of the loss tangent peak decreases as the isocyanate content of the prepolymer is increased. The peak maximum of the $\tan \delta$ curve is increased from 0.25 to 0.34 as the prepolymer isocyanate content is decreased from 4.5 to 3.6%.

The final compositional parameter to be investigated is the effect of the amount of curative used on the properties of the resultant polyurethane. A new PTMEG-based prepolymer with an isocyanate content of 4.05% was used in this study. Polyurethanes were made from this prepolymer using 90, 100, and 110 parts per hundred of DETDA as the curative. The properties of these resultant urethanes are summarized in Tables V and VI. It is clear that the change in amount of curative has almost no effect on the acoustic impedance of the resultant urethane. However, increasing the amount of curative causes a significant reduction in hardness and results in the formation of a urethane with much poorer mechanical properties. Samples suitable for dynamic mechanical testing were also prepared using the different amounts of curative. These samples were analyzed on the DMTA and the results are summarized in Figures 6 and 7. The dynamic Young's modulus is seen to decrease as the amount of curative is increased, which is consistent with the results of the tensile testing. It is clear from Figure 7 that a more significant change in the $\tan \delta$ occurs as the amount of curative is changed. Changing the amount of cu-

Table V Properties of Meta Tetramethyl Xylene Diisocyanate Based on Polyurethanes Cured with Varying Amounts of DETDA

Cure Stoichiometry	Hardness Shore A	Sound Speed (m/s)	Density (kg/m ³)	Acoustic Impedance (rayl)
90	72	1611	1.03×10^3	1.66×10^6
100	69	1613	1.03×10^3	1.66×10^6
110	57	1618	1.04×10^3	1.68×10^6

Table VI Tensile Properties of Meta Tetramethyl Xylene Diisocyanate Based on Polyurethanes Cured with Varying Amounts of DETDA

Cure Stoichiometry	Modulus (MPa) (600%)	Tensile Strength (MPa)	Ultimate Elongation (%)
90	17.7	24.8	650
100	12.8	18.3	700
110	7.6	9.8	832

rative from 90 to 110 pph results in the formation of a polyurethane with a significantly larger loss tangent at temperatures above -20°C . This effect has been confirmed in independent measurements made by the resonance technique. On the basis of these results, a mixing ratio of less than 100 pph of curative appears to be desirable due to the improved tensile properties and lower $\tan \delta$ values obtained in the resultant polyurethane.

Seawater Aging

The initial study of the weight gain caused by seawater exposure suggested that these urethanes possess good resistance to seawater exposure. To better assess the effect of seawater exposure on these urethanes, a more detailed study was performed in which the change in the mechanical and acoustical properties of these urethanes were determined after seawater exposure. This study was performed on two

urethanes based on the meta isomer of tetramethyl xylene diisocyanate. One urethane was obtained from a PPG-based prepolymer having an isocyanate content of 4.91%. The other urethane was obtained from a PTMEG-based prepolymer with an isocyanate content of 3.9%. Samples of these two urethanes were immersed in seawater for 12 weeks at temperatures of 25, 55, and 70°C . At each temperature, samples suitable for different types of testing were employed for both urethanes. During the course of the testing period, Shore A hardness and sound speed measurements were made after various aging times. Other properties such as Instron tensile testing, volume resistivity, and dynamic mechanical analysis were only measured at the end of the testing period. The changes in hardness and sound speed during the aging period are shown in Figures 8 and 9 for the PTMEG-based polyurethane. The Shore A hardness appears to decrease significantly at short aging times but is only decreasing slowly near the

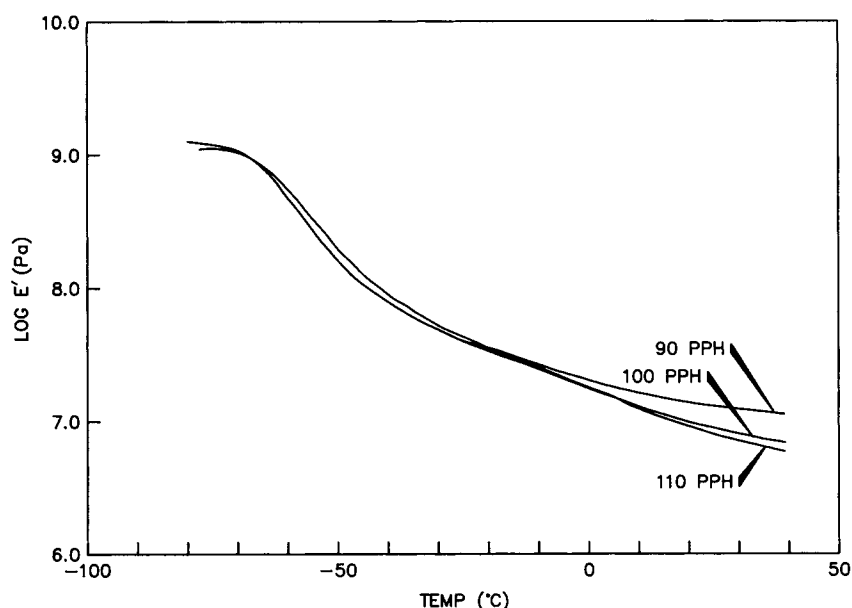


Figure 6 Plot of the dynamic Young's modulus as a function of temperature measured at 1 Hz for the urethanes with the indicated cure stoichiometries.

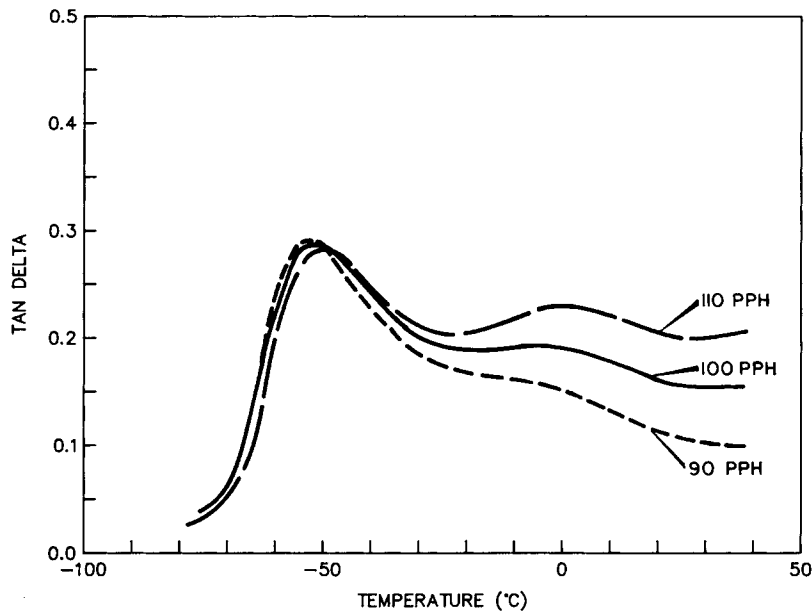


Figure 7 Plot of the loss tangent as a function of temperature measured at 1 Hz for the urethanes with the indicated cure stoichiometries.

completion of the aging period. The sound speed data has more scatter but is also changing very slowly by the end of the aging period. The PPG-based urethane was found to undergo similar changes in hardness and sound speed as a function of time. It therefore appears that 12 weeks is a sufficient aging time to determine if significant property

changes are induced in this urethane by seawater exposure.

The observed property changes induced in these two urethanes are summarized in Tables VII-IX. The specific acoustic impedance of the aged PTMEG-based urethane was actually closer to that of seawater than the original urethane. This is sim-

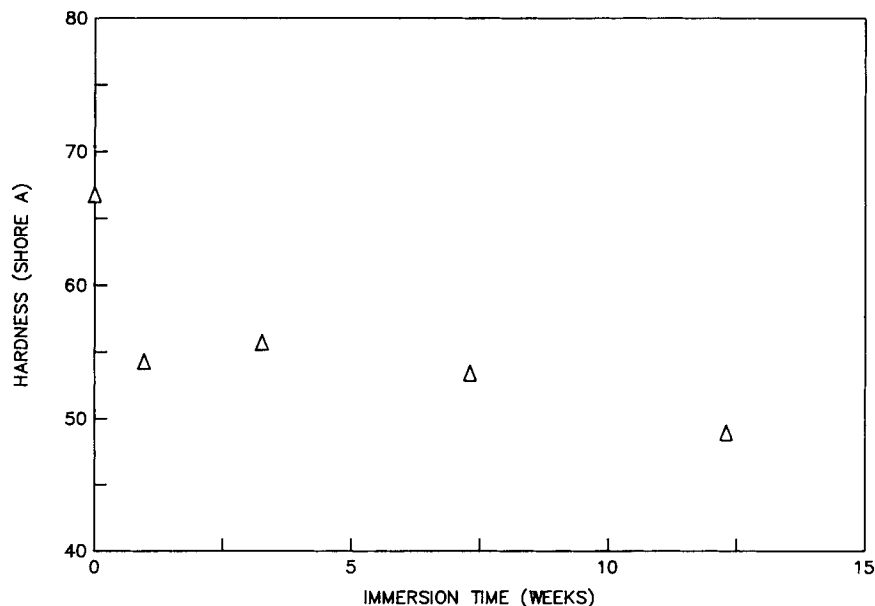


Figure 8 Plot of the Shore A hardness as a function of aging time at 70°C for a PTMG-based urethane.

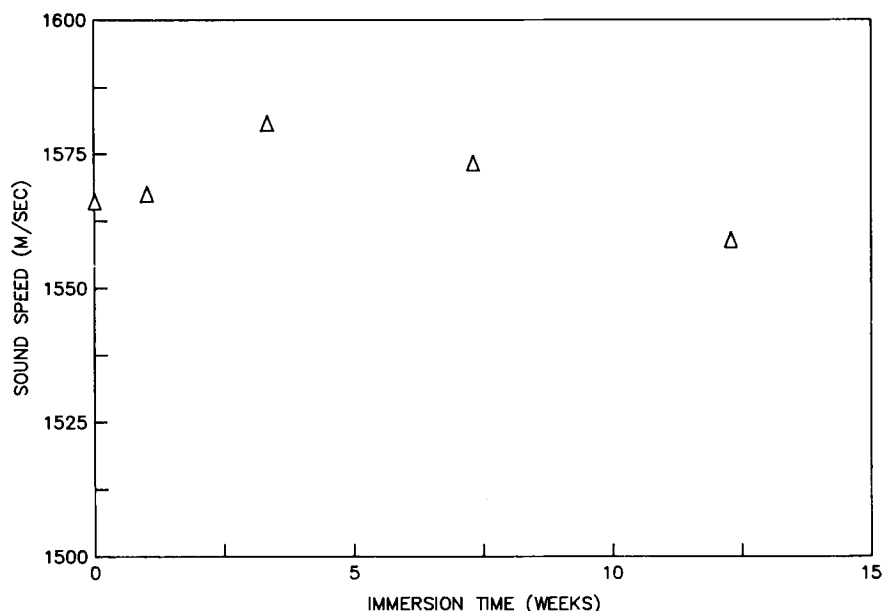


Figure 9 Plot of the sound speed as a function of aging time in seawater at 70°C for a PTMG-based polyurethane containing the meta tetramethyl xylene diisocyanate group.

ply due to the fact that the aging caused a reduction in sound speed. More important is the fact that the impedance is not significantly changed by the exposure even at the high temperature of 70°C. It is clear that the aging does cause a significant deterioration in the mechanical properties but even at the highest aging temperature the urethanes still have retained more than half their tensile strength. This resistance to aging is comparable to that typically observed in polyurethanes based on aromatic diisocyanates.¹² The volume resistivity was significantly affected by the exposure, but both urethanes still had an acceptable resistivity after the aging period. The reduction in volume resistivity is most likely

due to either ionic diffusion into the urethane or sample hydrolysis. Further experiments are needed to determine the relative importance of these mechanisms. The dynamic mechanical properties of the PTMEG-based urethane were measured on the DMTA subsequent to the aging period. It was found that a slight reduction in both the dynamic Young's modulus and the magnitude of the loss tangent peak were induced by the seawater exposure. No detectable shift in the position of the loss tangent peak occurred after the seawater exposure. These small changes in dynamic mechanical properties would not adversely affect the performance of the urethane as a transducer encapsulant.

Table VII Effect of Seawater Aging on the Properties of Polyurethanes Based on the Meta Tetramethyl Xylene Diisocyanate Group

Soft Segment	Aging Temperature (°C)	Sound Speed	Hardness Shore A	Impedance Deviation from Seawater (%)
PPG	Unaged	1533	73.2	1.56
PPG	25	1520	64.6	0.70
PPG	55	1515	61.6	0.37
PPG	70	1509	55.3	0.03
PTMG	Unaged	1566	66.6	0.81
PTMG	25	1561	61.3	0.74
PTMG	55	1561	55.5	0.61
PTMG	70	1559	49.2	0.40

Table VIII Effect of Seawater Aging on the Tensile Properties of Polyurethanes Based on the Meta Tetramethyl Xylene Diisocyanate Group

Soft Segment	Aging Temperature (°C)	300% Modulus (MPa)	Tensile Strength (MPa)	Ultimate Elongation (%)
PPG	Unaged	8.3	19.1	590
PPG	25	7.1	15.8	630
PPG	55	7.5	> 14.2	> 598
PPG	70	9.1	15.7	757
PTMG	Unaged	4.2	> 14.7	> 790
PTMG	25	4.5	> 14.7	> 820
PTMG	55	5.2	> 16.0	> 812
PTMG	70	5.0	10.9	996

Bondability Experiments

In addition to desirable properties and good seawater resistance, it is important for an encapsulant to form a good bond to the stainless steel surface of the transducer. There are primer systems available that give good bondability between stainless steel and urethanes based on aromatic isocyanates. Aliphatic isocyanates are less reactive than aromatic isocyanates, and as a result the same primer systems may not be appropriate. Nonetheless, the primer system PRC-420, known to work well with aromatic isocyanate urethanes, was initially tried. In a study of commercial urethanes based on the aromatic isocyanate, toluene diisocyanate, peel strengths in excess of 7.0 kN/m were obtained with this primer.¹² More importantly, failure was found to occur by rupture within the urethane rather than at the urethane-primer bond line. This observation indicates that the urethane and primer are forming true chemical links. The actual peel strength values are simply reflecting the strength of the urethane itself. The present bondability study was performed using a PTMEG-based prepolymer containing 3.9% of the meta isomer of tetramethyl xylene diisocyanate. The urethane was cured with 100 pph of DETDA on a

stainless steel substrate coated with the PR-420 primer. In the subsequent Instron peel test, failure was found to occur at the urethane-primer bond line and a very low average peel strength of 1.8 kN/m was obtained. A second set of urethanes were cured over this primer. The primer was first heated to 100°C for an hour before the urethane was applied. This heating was done in an attempt to activate the isocyanates in the primer, which are bound to blocking agents at room temperature. This modification was found to significantly improve the bondability of these polyurethanes. In subsequent peel tests the average peel strength was found to be 11 kN/m. However, failure was still found to occur at the bond line rather than by rupture within the urethane. Increasing the amount of curative to 110 pph increased the peel strength even further to a value of 18.9 kN/m, but failure still occurred at the bond line.

Although these peel strengths are probably adequate, the fact that failure occurred at the bond line indicates that an even higher peel strength can be achieved if a better bond is obtained. Therefore, bondability tests were performed using a series of other commercial primers. The best results were obtained with Chemlock 213, a new product being

Table IX Effect of Seawater Aging on the Volume Resistivity of Polyurethanes Based on the Meta Tetramethyl Xylene Diisocyanate Group

Aging Temperature (°C)	Volume Resistivity (Ω-cm)	
	PTMG Polyurethane	PPG Polyurethane
Unaged	3.4×10^9	1.9×10^{11}
25	3.6×10^9	—
70	7.3×10^8	7.0×10^8

marketed by the Lord Corporation. With this primer, failure did occur within the urethane and an average peel strength of 31.5 kN/m was obtained.

CONCLUSIONS

The excellent seawater resistance and favorable acoustic properties indicate that these polyurethanes based on the meta isomer of tetramethyl xylene diisocyanate and polytetramethylene glycol are promising candidates as transducer encapsulants. The compositional study indicates that these urethanes can be optimized to have low dynamic loss or a very close impedance match to seawater while maintaining adequate physical and mechanical properties.

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