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Polyurea and Polyurea Composites for Stress-wave Energy Management

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Polyurea and Polyurea Composites for Stress-wave Energy Management

A Dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy

in

Engineering Science (Mechanical Engineering)

by

Zhanzhan Jia

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2016
The Dissertation of Zhanzhan Jia is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

University of California, San Diego

2016
DEDICATION

To my family and friends.
Devotion to the truth is the hallmark of morality; there is no greater, nobler, more heroic form of devotion than the act of a man who assumes the responsibility of thinking.

—Ayn Rand
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CONFERENCE PUBLICATIONS


BOOK CHAPTER

ABSTRACT OF THE DISSERTATION

Polyurea and Polyurea Composites for Stress-wave Energy Management

by

Zhanzhan Jia

Doctor of Philosophy in Engineering Science (Mechanical Engineering)

University of California, San Diego, 2016

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Mechanical properties of elastomeric polymers are highly sensitive to the loading rate, temperature and pressure in their transition zone between glassy state and rubbery state. This study focuses on polyurea, which is a group of elastomeric copolymer which has excellent thermal and mechanical properties. It is environmentally stable, tough, abrasion-resistant and dissipative. Both its storage and loss moduli increase significantly when the strain rate increases in the transition zone. This property gives great potential for polyurea to manage mechanical energy in various loading conditions. When applied as a coating material, it can significantly increase
the structure’s resistance to the shock or blast loading. Its dissipative nature can also 
be applied to design composite materials that have excellent properties. Its transi-
tion zone spans in a wide frequency range, which can be more than 10 decades in the 
logarithmic scale.

Even though various types of polyurea are widely applied, the mechanical 
properties of polyurea are not fully understood in such a wide frequency range. 
This research studies polyurea from various perspectives and provides knowledge of 
polyurea and its composites in terms of fabrication, characterization in various fre-
quency ranges, modeling and the interface study of polyurea composites, as listed in 
the five parts:

1. Understanding polyurea, the effect of molecular structure and the stoichio-
metric ratio on its dynamic mechanical properties.


3. A computational code to efficiently and effectively obtain constitutive mod-
els for polyurea and its composites in a wide frequency range.

4. Modification, characterization and modeling of the interfaces of polyurea 
composites.

5. A novel testing technique for directly characterizing the viscoelastic prop-
erties of polyurea and its composites at mid-level (kHz) frequencies, which fills the 
frequency gap between dynamic mechanical testing and ultrasonic wave measurement.
Chapter 1

Introduction of the dissertation
and various types of polyurea

1.1 Introduction of the dissertation

Polyurea is a group of copolymer synthesized by the reaction of a diamine and a diisocyanate. Polyurea elastomers are light-weight, environmentally-stable, water-proof, tough, abrasion-resistant and are capable of dissipating energy in a wide frequency range. Its mechanical properties change when temperature, pressure or strain rate changes.

Polyurea are widely applied as a coating material to reinforce the structures that are subject to dynamic loading. For example, experiments have shown that a coating of polyurea on the back of a steel plate can significantly increase its resistance to the impact loading [2]. It also can be applied as a construction material to strengthen the building walls against earthquakes [67]. The excellent properties of polyurea are believed to be related to the fact that it is a tough material, and
both its storage and loss moduli increase significantly when the frequency or pressure increases [63, 60, 36].

In this research we used Versalink (Air Products and Chemicals, Inc.) and Isonate 143L (The DOW Chemical Company) to synthesize polyurea. Versalink is a product line of diamine curatives with various molecular weights and chain lengths. The molecular structure of Versalink is shown in Fig. 1.1. Isonate 143L is a polycarbodiimide-modified diphenylmethane diisocyanate. The molecular structure of which is shown in Fig. 1.2.

Even though polyurea has been widely applied and its advantages have been experimentally observed, this material is not fully understood comparing to many other structural materials, due to the complex nature of its viscoelasticity, which is sensitive to frequency, temperature and pressure in a wide range.

In this research, we want to know how the molecular structure or how the stoichiometric ratio of polyurea affects its thermal and mechanical properties. In the micro scale, we seek to modify material properties by composition for polyurea
composites to have excellent properties, such as high storage and loss modulus, or low density and mechanical robustness. In terms of characterizing the viscoelastic properties of polyurea and its composites, our existing characterization techniques are not able to cover such a wide frequency range in a direct measurement. At the low frequency end, viscoelastic properties can be measured by dynamic mechanical analysis (DMA), which tests between $10^{-2}$ to $10^{2}$ Hz according to TA Instruments. For the high frequency end, ultrasonic wave measurement spans from a little less than 50 kHz to 200 MHz [74]. But the relaxation of polyurea is from $10^{-5}$ to $10^{10}$ Hz [56, 35]. Thus it raises questions, such as how to reliably estimate the viscoelastic properties of polyurea in a wide frequency range using experimental data tested in a limited frequency range, and whether it is possible to design new testing techniques to fill the frequency gaps in between the existing techniques.

These questions are not exclusive for polyurea, they also exist for many other elastomers in their transition zones between glassy state and rubbery state. Thus the methodology and results of this research also provide useful information for studying other similar elastomers and composites.

In this dissertation, researches have been conducted around polyurea and its composites, including fabrication, characterization, viscoelastic modeling, interface study, novel characterizing techniques for polyurea and polyurea composites. The structure of this dissertation is organized as the 5 chapters.

- Chapter 1: Introduction of polyurea and understanding the effect of molecular structure and the stoichiometric ratio on its dynamic mechanical properties.
- Chapter 2: Novel polyurea-based composite materials.
- Chapter 3: A computational code for effectively and efficiently obtaining consti-
tutive models that cover a wide frequency range for polyurea and its composites.

- Chapter 4: Modification, characterization and modeling of the interfaces of polyurea composites.

- Chapter 5: A novel testing technique for directly characterizing the viscoelastic properties of polyurea and its composites at mid-level frequency (kHz).

Chapter 1 is the introduction of polyurea. It also discusses the thermal and dynamic mechanical properties of various types of polyurea with varied molecular structures or stoichiometric ratios. The structure-property relation of polyurea is discussed in terms of the molecular structure effect and the stoichiometric ratio effect on the mechanical properties of polyurea.

Chapter 2 introduces two types of novel polyurea composites. These two types of polyurea composites have been used for developing a layered composite materials for underwater sonar stealth utilizing their excellent properties.

Chapter 3 discusses the constitutive modeling of polyurea and polyurea composites. This chapter answers the question about how to efficiently and reliably approximate the mechanical properties of polyurea and polyurea composites in the wide frequency range when the direct measurements are not available. A computational code have been developed to calculate the relaxation modulus and Prony series of polyurea and its composites which can be directly used in the computational platforms. Prony series of polyurea and various types of polyurea composites are provided at the end of the chapter.

Chapter 4 is about the polyurea-glass interface and polyurea-metal interface. Modifying the interfacial bonding is discussed for creating weak, intermediate or
strong bonding. Characterization and modeling methods for the interfaces are also discussed. This part of research provides knowledge for modifying, characterization, and modeling the interfaces for polyurea composites.

Chapter 5 is about a novel characterization technique for directly measuring the viscoelastic properties of polyurea and its composites at the mid-level (kHz) frequencies, which fills the gap between the testing frequency of dynamic mechanical analysis and ultrasonic wave measurement.

1.2 Understanding polyurea: the effect of molecular structure

In order to better understand the dynamic mechanical properties of polyurea, both the effect of chain length and the effect of stoichiometric ratio on the thermal and mechanical properties of polyurea have been studied to provide guidance for the optimal polyurea or polyurea composite design for various loading frequencies.

Versalink P-250, Versalink P-650 and Versalink P-1000 are oligomeric diamines products of Air Products and Chemicals, Inc.. The product number indicates the approximate molecular weight of the diamine, which is related with the polymer chain length of the resultant polyurea, i.e. “m” is varied in Fig. 1.1 for Versalink P-250, Versalink P-650 and Versalink P-1000. The synthesized polyurea is named using its Versalink type. For example, PU-P1000 represents polyurea fabricated using Versalink P-1000, and PU-P650 represents polyurea fabricated using Versalink P-650.

Both PU-P650 and PU-P1000 have micro-phase separation, they have hard domains dispersed in the soft domain matrix [13]. However, PU-P250, due to the
short chain length of the Versalink P-250, it does not have discernible phase separation [13]. For PU-P650 and PU-P1000, the hard domains are mainly composed of Isonate 143L and the soft domain is mainly composted of Versalink. Different from PU-P1000 and PU-P650, PU-P250 is glassy and brittle at room temperature.

In this part of study, only PU-P1000 and PU-P650 are characterized since they are two types of elastomers which have wide transition zones between the glassy state and rubbery state for the temperature and frequency range of polyurea applications.

The knowledge obtained from this part of study can be used as a guidance for polyurea selection and property tuning in designing polyurea and polyurea-based composite materials.

1.2.1 Material fabrication

The fabrication of PU-P650 uses the diamine component Versalink P-650 and the diisocyanate component Isonate 143L; the fabrication of PU-P1000 uses Versalink P-1000 and Isonate 143L. Versalink P-1000 and P-650 are yellow-colored viscous liquids at room temperature. Isonate 143L is a polycarbodiimide-modified diphenylmethane diisocyanate which is a less viscous yellow liquid at room temperature comparing to Versalink P-1000 and P-650. The fabrication procedures of PU-P1000 and PU-P650 are very similar, only that the curing speed of PU-P650 is faster than PU-P1000, which requires a shorter mixing and molding time for PU-P650.

In the fabrication, Versalink and Isonate 143L are first degassed in the vacuum at 1 torr for 1 hour until most of the air bubbles are removed. The two components are degassed using the setup shown in Fig. 1.3. The Isonate 143L is degassed in the left-hand side flask, while Versalink is degassed in the right-hand side reaction
flask. At the same time, the two components are stirred using Teflon coated magnetic stir bars. After the degassing process, Isonate 143L is added into Versalink, and the mixture is stirred and degassed for another 5 minutes under the vacuum. Then the resultant mixture is transferred into various Teflon molds to make samples for various tests, as shown in Fig. 1.4. The total handling time before the materials get too viscous is around 15 minutes for PU-P1000 and 10 minutes for PU-P650 after adding Isonate 143L into Versalink. The stoichiometric ratio is controlled at 1.05 for both PU-P1000 and PU-P650 [10]. The 5% excess of isocyanate is to ensure the completion of polymerization. The cast polyurea samples are cured in the environmental chamber for at least 2 weeks before testing. The relative humidity in the chamber is control at 10%.

For consistent polyurea properties, care needs to be taken for storing Isonate 143L, since it is quite sensitive to humidity and temperature. Reaction with water can reduce the number of viable functional groups in Isonate 143L; higher temperature will accelerate this deterioration and lower temperature will cause it to crystallize. In our lab, Isonate 143L is stored in a dry vacuum bag and is kept in an incubator with temperature controlled at 25°C. Versalink is a much stabler chemical comparing to Isonate 143L and does not require a special storage condition.

1.2.2 Characterization: dynamic mechanical analysis (DMA)

Viscoelastic properties of polyurea are tested by single cantilever bending on TA 2980 dynamic mechanical analyzer. In this dissertation, single cantilever bending test is most commonly used, as shown in Fig. 1.5. Single cantilever mode relaxes the axial stress in the sample due to the thermal expansion or contraction thus is
Figure 1.3: Polyurea fabrication setup. The flask on the left-hand side is for Isonate 143L degassing and the reaction flask on the right-hand side is for Versalink degassing.

Figure 1.4: Polyurea samples cast in Teflon molds. The samples in the top-left mold are for ultrasonic tests; the square-shaped sample on the bottom left is for the hardness testing and the long strip on the right is for dynamic mechanical analysis (DMA) single cantilever bending test.
the preferred testing mode. The nominal size of the polyurea sample for the single-cantilever bending DMA test is $3\text{mm} \times 10\text{mm} \times 30\text{mm}$. The span between the fixed clamp and the movable clamp is $17.5\text{mm}$.

From DMA single-cantilever bending test, storage and loss Young’s moduli can be calculated from the test data using the corresponding TA data analysis software. As in Eq. 1.1, the complex Young’s modulus has two parts $E'$ and $E''$. The real part $E'$ is the storage modulus, representing the capability of the material to store elastic energy, while the imaginary part $E''$ is the loss modulus, representing the capability of the material to dissipate mechanical energy into heat, Eq. 1.1. The ratio of $E''/E'$ is the $Tan\delta$, which represents the ratio of the dissipated energy to the stored elastic energy in each loading cycle. For polyurea elastomers, $E^*$ has both the storage and loss moduli, and both the storage and loss moduli are highly sensitive to the temperature, pressure and strain rate.

$$E^* = E' + iE''$$ \hspace{1cm} (1.1)

For polyurea elastomers, the sweep frequencies of DMA tests are 20, 10, 5, 2 and 1 Hz, and the testing temperature range is $-80^\circ\text{C} \sim 50^\circ\text{C}$, with $3^\circ\text{C}$ increments. The amplitude of the mover clamp displacement is $15\ \mu\text{m}$. Liquid nitrogen is used to cool the system to sub-ambient temperatures. This temperature range includes the glass transition temperature and most of the transition zone of polyurea elastomers. At each testing temperature, the frequency sweep starts from the highest frequency $20\ \text{Hz}$ and steps down to the lower frequencies.

For higher temperatures, such as room temperature or higher, the young’s modulus of polyurea is dominated by its shear modulus, and is around three times of
Figure 1.5: Dynamic mechanical analysis single cantilever bending test setup

its shear modulus.

If the sample could not be made big enough to meet the requirements of single cantilever bending test, DMA tension test could be conducted for small polyurea samples. The size requirements for each test could be found on the user manual of TA 2980 [72]. The test results from single-cantilever bending test and tension test matched well with each other for polyurea.

TA 2980 also has a set of shear-sandwich test grip designed to directly measure the frequency dependence of shear modulus. However, shear-sandwich test has never been used for characterizing the shear properties of polyurea and its composites in this dissertation. The reason and analysis can be found in Appendix A.
1.2.3 Characterization: modulated differential scanning calorimetry (MDSC)

A modulated differential scanning calorimeter (TA instrument DSC 2920) is used to characterize the glass transition temperature of polyurea, as shown in Fig. 1.6. The Glass Transition Temperature ($T_g$) is one of the most important properties of polymers, since polymers behave very differently below or above this temperature. Below $T_g$, polymers are glassy, and above $T_g$, polymers become soft and rubbery.

The modulated differential scanning calorimetry separates the total heat flow of DSC into two parts. One part is related with the heating rate, and the other part is independent of the heating rate, as in Eq. 1.2 [40]. The part of heat flow related with heating rate is the reversing heat flow and the part not related with the heating rate is the non-reversing heat flow. The reversing heat flow curve measures the heat capacity and the non-reversing curve measures the kinetic part of the thermal change like enthalpic recovery, evaporation, crystallization etc [71].

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)$$ (1.2)

During the test, one sample pan and one reference pan are used. As in Fig. 1.6, on the top left of the figure is the detail of the test cell, where the two silver-colored pans are standard aluminum test pans. The one on the top is the sealed reference pan the the one on the bottom is the sealed sample pan. The difference of the heat flow between the two pans are recorded by the calorimeter. The weight difference between the sample pan and the reference pan is controlled to be less than 0.02 mg, and the sample weighted between 15-20 mg is put in the sample pan. The
difference of the heat flow between the two pans is the total heat flow, which is later on separated into the heating-rate-dependent part and the heating-rate-independent part.

The temperature range of the DSC test for polyurea is set between $-100^\circ C \sim 220^\circ C$. The testing cell is first equiliteral at $-100^\circ C$, then ramped up to $220^\circ C$, with the average heating rate being $3^\circ C/\text{min}$, and is modulated $+/-1.000^\circ C$ every 60 seconds. Liquid nitrogen is used to cool the sample to sub-ambient temperatures, and nitrogen purge gas in the flow rate of $50\text{ml/min}$ is used to protect the testing cell. Usually two tests are conducted in succession to monitor any change in the sample due to the thermal cycle.

The glass transition can be measured from the reversing heat signal. When the polymer is changing from the glassy state to the rubbery state, the heat capacity of the polymer changes. Below glass transition there is only vibration of the polymer chain; during the glass transition, there is vibration and rotation of the polymer chain; above the glass transition, the polymer chain can slide against each other [1]. The heat capacity increases when the mobility of the polymer chain increases. Thus at glass transition temperature, there is a step in the reversing heat flow. The glass transition temperature can be measured on the corresponding TA data processing software on the heat flow curves, as in Fig. 1.7.

### 1.2.4 The effect of the chain length of the diamine component on the glass transition temperature

The curves of the reversing heat flow of MDSC tests of PU-P650 and PU-P1000 are shown in Fig. 1.7. The glass transition temperature ($T_g$) of PU-P1000
Figure 1.6: TA DSC 2920. The detail of the testing cell is shown on the top left of the picture.

is at $-60^\circ$C and the $T_g$ of PU-P650 is at $-40^\circ$C. This $T_g$ is the glass transition of the soft domain of polyurea, which is mainly composed of the diamine component. The glass transition of the hard domain is above 140$^\circ$C for polyurea [57], which is above the usual application temperature for polyurea, thus the hard domain can be considered as rigid inclusions for most polyurea applications, since it is rigid and glassy for most application temperatures.

The difference of $T_g$ between PU-P650 and PU-P1000 is due to the difference of the chain length of the two diamines that are used to synthesize these two types of polyurea. The longer the chain length of the polyurea, the lower the glass transition temperature of the soft domain. This trend is also true for PU-P250. The chain length of Versalink P-250 is the shortest among the three types of diamine curatives and the $T_g$ of PU-P250 is the highest. $T_g$ of PU-P250 is higher than room temperature, thus PU-P250 is rigid and glassy at room temperature.

Knowing the effect of the diamine chain length on the glass transition temperature of polyurea, the polyurea elastomer’s $T_g$ can be tuned by changing the chain
Figure 1.7: MDSC reversing heat flow of PU-P1000 and PU-P650. The glass transition temperatures ($T_g$) of PU-P1000 is around $-60^\circ C$, and the $T_g$ of PU-P650 is around $-40^\circ C$.

length in the soft domain.

1.2.5 The effect of the chain length of the diamine component on the dynamic mechanical properties

DMA single cantilever tests were conducted for PU-P650 and PU-P1000 samples at frequencies 1, 2, 5, 10, 20 Hz and in the temperature range of $-80^\circ C \sim 50^\circ C$.

The results at 1 Hz are shown in Fig. 1.8-1.10. For clarity, only DMA data tested at 1 Hz are shown in the plot while data of other frequencies all have similar trend. These plots indicate that changing the chain length of the diamine component also changes the viscoelastic properties of polyurea.

As can be seen in Fig. 1.8, PU-P650 is stiffer than PU-P1000 at temperatures
above $-65^\circ$C. In Fig. 1.9, the peaks of the loss modulus for both types of polyurea are located around their glass transition temperature, which is around $-60^\circ$C for PU P-1000, and $-40^\circ$C for PU-P650. Fig. 1.10 shows $\tan\delta$ for each type of polyurea at 1Hz. The plot of $\tan\delta$ shows that, below $-15^\circ$C, PU-P1000 dissipates a larger percentage of energy than PU P-650; and PU-P650 is more dissipative for higher temperatures. In other words, the peak of the loss modulus shifts to higher temperature when the chain length of polyurea decreases.

Knowing the effect of the diamine’s chain length to the dynamic mechanical properties of polyurea helps us to choose the best diamine curative when certain dynamic mechanical properties are required. For example, at low frequencies (100 Hz), PU-P650 is stiffer and more dissipative at room temperature, and PU-P1000 is more dissipative below $-10^\circ$C.
Figure 1.9: Loss Young’s modulus of PU-P1000 and PU-P650 tested at 1Hz from $-80^\circ C$ to $50^\circ C$.

Figure 1.10: Tanδ of PU-P1000 and PU-P650 tested at 1 Hz from $-80^\circ C$ to $50^\circ C$. 
1.3 Understanding polyurea: the effect of the stoichiometric ratio

Theoretically, the isocyanate component and amine component must be mixed in a stoichiometric ratio of 1:1. Most polyurea formulations are calculated to overindex the isocyanate component of the system on the order of 1.05, i.e. a five percent excess of the isocyanate component is used beyond the 1:1 stoichiometric ratio for a complete reaction [10], this excess isocyanate also helps account for the lost isocyanate in the reaction with moisture during storage or application.

In order to study the sensitivity of polyurea to the stoichiometric ratio of the isocyanate and amine, PU-P1000 samples of 7 stoichiometric indices were fabricated, the 7 indices were 0.9, 0.95, 1.00, 1.05, 1.10, 1.15 and 1.20. DMA and MDSC tests were conducted to study the effects of the stoichiometric ratio on the mechanical and the thermal properties of polyurea.

1.3.1 The effect of the stoichiometric ratio on the glass transition temperature

From the reversing heat flow of the MDSC data, glass transition temperature of polyurea is measured, as shown in Fig. 1.11. $T_g$ is measured on the corresponding data analysis software of DSC 2920, and it is the center temperature of the whole glass transition process, which is the step showing on the curve of the reversing heat flow. The vertical axis number is not of interest here. For clearly showing each curve, the reversing heat flow curves are shifted vertically to avoid overlapping with each other. Fig. 1.11 shows that all the stoichiometric indices have the same $T_g$ as the
Figure 1.11: MDSC reversing heat flow data of PU-P1000 with various stoichiometric indices. The isocyanate to amine stoichiometric ratios are 0.90, 0.95, 1.00, 1.05, 1.10, 1.15, 1.20.

standard stoichiometric ratio 1.05, which is at around $-60^\circ$C. The result shows the level of the isocyanate does not change $T_g$ of PU-P1000.

1.3.2 The effect of the stoichiometric ratio on the dynamic mechanical properties

DMA test was conducted for PU P-1000 samples fabricated with the 7 stoichiometric ratios using single-cantilever bending tests, and Young’s modulus was measured at 1, 2, 5, 10, 20 Hz from $-80^\circ$C to $50^\circ$C.

As shown in Fig. 1.12, both the storage and loss modulus increases at high temperatures when the stoichiometric ratio increases. In order to clearly show the
Figure 1.12: Storage and loss moduli of PU-P1000 of various stoichiometric ratio: 0.90, 0.95, 1.00, 1.05, 1.10, 1.15, 1.20.

difference, data of each stoichiometric ratio measured at 1 Hz is normalized with respect to the standard index 1.05, as shown in Fig. 1.13. These two plots indicate that polyurea’s mechanical property is sensitive to the stoichiometric ratio of the isocyanate and amine. Both its storage and loss moduli increase when the stoichiometric index increases from 1.05 to 1.20 for temperatures higher than $T_g$. For example, 20% more isocyanate can increase both storage and loss moduli of PU P-1000 up to 1.8 times comparing to the stoichiometric index 1.05. $Tan\delta$ of each stoichiometric index (Fig. 1.14), shows that lower stoichiometric ratio dissipates a larger proportion of energy in dynamic loading within the temperature range $[T_g, T_g + 40^\circ C]$.

The explanation for the effects of stoichiometric ratio is related with the content of hard domains in the polyurea. The hard domains of polyurea are mainly composed of Isonate 143L [58], thus reducing the stoichiometric ratio means reducing the volume fraction of the hard domains, which has a high $T_g$ [57] and could be regard as non-dissipative elastic inclusions and chemical and physical crosslink
Figure 1.13: Relative storage and loss modulus comparing to stoichiometric index 1.05.

Figure 1.14: $\tan \delta$ of PU-P1000 for the 7 stoichiometric ratios between 0.9 to 1.2.
sites that constrained the mobility of the polymer chains [52]. Physical crosslinks means the constraints on polymer chains are not by covalent bonds, comparing to the chemical crosslinks. Thus increasing the stoichiometric index increases the stiffness of polyurea, but reduces its $\tan\delta$, which is the ratio of the dissipated energy to the stored elastic energy in polyurea.

This part of study provides knowledge regarding the effect of the hard domains and the crosslink sites to the thermal and mechanical properties of polyurea, and provides guidance on fine-tuning the properties. The result shows that it is important to keep the stoichiometric ratio accurate in the fabrication process in order to make different batches of polyurea have comparable properties. As a result of this part of research, a fluctuation of stoichiometric ratio within $\pm0.5\%$ is controlled for all polyurea fabrications for all the polyurea samples in this dissertation.

1.4 Summary

In this chapter, the thermal and mechanical properties of two types of polyurea (PU-P650 and PU-P1000), and the sensitivity of polyurea to the stoichiometric ratio were studied.

The DMA testing result shows that the longer chain length in the soft domain of polyurea makes PU-P1000 softer in general but more dissipative at low temperatures that are close to $T_g$, while shorter chain length in the soft domain of PU-P650 gives both higher storage and loss moduli in general except for the low temperatures that are close to $T_g$. Knowing the effect of the diamine chain length to the viscoelastic properties of polyurea enables us to choose the right material for specific application temperatures or frequencies.
The stoichiometric ratio study shows that the viscoelastic properties of polyurea is very sensitive to the ratio of isocyanate to amine. Higher stoichiometric ratio gives both higher storage and loss moduli and lower stoichiometric ratio gives both lower storage and loss moduli. Slightly altering the stoichiometric ratio could be used to fine-tune the properties of polyurea. For different batches of polyurea to be comparable, the stoichiometric ratio needs to be strictly controlled.


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Chapter 2

Novel polyurea composites

Various types of novel polyurea composites have been developed at CEAM. In this chapter, two types of novel polyurea composites are discussed. They are polyurea with milled glass (PUMG) and polyurea with phenolic microbubbles (PUPMB). The matrix material of the two types of polyurea composites is PU-P1000. Milled glass is micron-size short glass fibers and phenolic microbubbles are micron-size hollow phenolic spheres. Both of them are affordable filler materials. These particle inclusions can significantly change the storage and loss moduli of the resultant composites or alter their densities and acoustic impedance. These two types of composites have been used to design layered composite materials for under water sonar stealth. Both of them are considered light-weight materials comparing to other structural materials, such as steel or aluminum. PUMG is a polyurea composite that has both high storage and loss moduli, and PUPMB has low density and low acoustic impedance. This chapter will discuss their fabrication and viscoelastic properties.
2.1 Polyurea composite material with high storage and loss moduli

PUMG with various volume fractions of milled glass was fabricated and tested by DMA single cantilever bending test. The effect of the milled glass volume fraction on the overall dynamic mechanical properties of polyurea composites was studied. The results showed that milled glass significantly increased both the storage and loss moduli of the resultant composite material.

2.1.1 Fabrication of polyurea with milled glass (PUMG)

Milled glass was added into the polyurea matrix to increase both the storage and loss moduli of the resultant composite material. The specific type of milled glass used in this study was the 3032 milled glass purchased from Fibertec, Inc. Milled glass 3032 is low-cost cylindrical short glass fibers. The average diameter is 16\(\mu\)m, and the average length is 200\(\mu\)m. The glass type is E-glass, and the particle density is 2.5g/cm\(^3\). Milled glass looks like white powder as received, but under microscope they are as in Fig. 2.1 (a). Care needs to be taken when handling the milled glass since it is very hazardous to inhale. The length distribution (Fig. 2.1) of the milled glass is in Fig. 2.1 (a).

During fabrication, the milled glass was first mixed with the more viscous component Versalink P-1000 thoroughly before degassing to prevent the milled glass from blowing away when pulling the vacuum. After degassing at 1 torr for 2 hours, until most of the air bubbles were removed from the two components, the precise amount of Isonate 143L was added into the Versalink-milled glass mixture and stirred using
magnetic stir bar for another 5 minutes. The resultant mixture was then transferred into the Teflon molds using disposable syringes. The samples were taken out of the Teflon molds after 24 hours and cured in the environmental chamber for at least two weeks before testing. In the environmental chamber, the relative humidity was controlled at 10%. PUMG composites with milled glass volume fractions of 10%, 15% and 20% were fabricated.

2.1.2 Scanning electron microscopy (SEM) of PUMG

The fractured surface of PUMG composite was observed under electron scanning microscope, as shown in Fig. 2.2. For preparing the fractured surface for SEM, PUMG composite was first scored on the surface using a razor blade, then it was soaked in the liquid nitrogen until temperature equilibration was reached. When temperature equilibrated with liquid nitrogen, PUMG sample became brittle and could be broken by two clamps from the notch. As can be seen from the fractured surface in Fig. 2.2, milled glass fibers were randomly distributed in the matrix in all orientations, and the fiber extrusion was due to the interfacial debonding between glass and polyurea.

The bonding strength between polyurea and glass can be modified using silane surface treatments on the milled glass surface, which will be discussed in Chapter 4.

2.1.3 Dynamic mechanical properties of PUMG

The incorporation of the milled glass into the polyurea matrix significantly changed the dynamic mechanical properties of PUMG. Both the storage and loss moduli were significantly increased by adding a small amount of milled glass.
Figure 2.1: (a) Microscopic picture of #3032 milled glass, and its (b) length distribution.
Dynamic mechanical analysis (DMA) single cantilever bending tests were conducted on TA 2980 for PUMG composites (milled glass volume fractions of 10%, 15% and 20%). The average DMA result was taken from two samples in the same batch for each volume fraction. The temperature range of the DMA tests was from $-80^\circ\text{C}$ to $50^\circ\text{C}$, with $3^\circ\text{C}$ increments. The test frequencies were 1, 2, 5, 10, 20 Hz.

For clarity, the DMA results are only shown for the 1 Hz and 20 Hz data. All the other frequencies show the same trend and are in between the data of 1 Hz and 20 Hz. Fig. 2.3 and 2.4 are the storage and loss moduli of the PUMG composites, and Fig. 2.5 is the Tan$\delta$ of each volume fraction of PUMG composites. In order to clearly show the difference of storage and loss moduli between various milled glass volume fractions, the ratios of the storage and loss moduli with respect to pure polyurea are plotted in Fig. 2.6, which clearly indicates that milled glass significantly increased both the storage and loss moduli of PUMG composites.
Figure 2.3: \( E' \) of PUMG composites with milled glass volume fractions of 10\%, 15\% and 20\%, tested at 1 Hz and 20 Hz.

Figure 2.4: \( E'' \) of PUMG composites with milled glass volume fractions of 10\%, 15\% and 20\%, tested at 1 Hz and 20 Hz.
2.1.4 Discussion on PUMG

As shown in Fig. 2.6, for high temperatures above 5°C, the storage and loss moduli of PUMG increases to about 2, 2.6, and 4 times respectively, for the 10%, 15% and 20% milled glass volume fractions comparing to the pure polyurea. It should be noted that for temperatures above 5°C, $\tan\delta$ does not drop when the milled glass volume fraction increases, as shown in Fig. 2.5, which means when the milled glass volume fraction increases, PUMG composite becomes stiffer, while it can still dissipate the same proportion of energy in each loading cycle. One possible explanation to this is when temperature is high enough, the compliance of the polyurea matrix increases such that the small deformation of the composite in the dynamic mechanical testing is dominated by the deformation in the polyurea matrix, therefore $\tan\delta$ of the composite is dominated by the $\tan\delta$ of the polyurea matrix. The peak of the loss modulus indicates the glass transition in the material. As can be seen in Fig. 2.4, the peaks
Figure 2.6: Relative $E'$ (a) and $E''$ (b) of PUMG composites with milled glass volume fractions of 10%, 15% and 20%, tested at 1 Hz. Each volume fraction is divided by the storage or loss Young’s moduli of pure polyurea respectively.
of $E''$ are around $-60^\circ$C, which is consistent with the measurement by differential scanning calorimetry (DSC) for pure polyurea [30]. More precisely, for higher milled glass volume fractions, the peaks shift lightly towards higher temperature, which indicates that higher volume fraction of the milled glass gives more constraint to the motion of the polymer chain.

2.2 Polyurea composite material with low density and acoustic impedance

The goal of this part of work is to develop a dissipative, low-density and low-impedance novel structural material that is also tough, environmentally stable, and capable of bearing pressure up to 10MPa without significant change in the impedance. Thus it can be used as a one component for designing a layered composite material for underwater sonar stealth to bring down the acoustic impedance of the whole layered structure to match with water. Polyurea with phenolic microbubbles (PUPMB) is such a material that satisfies these requirements.

2.2.1 Fabrication of polyurea with phenolic microbubbles (PUPMB)

Phenolic microbubbles are thin-shell microbubbles with the shell made of phenolic resin. The phenolic microbubbles used in this study is purchased from Fibertec, Inc. The average diameter of phenolic microbubbles is 37 $\mu$m, and the average shell thickness is 1 $\mu$m. The particle density is 0.23g/cm$^3$. A microscopic picture of the phenolic microbubbles and the size distribution is shown in Fig. 2.7.
Figure 2.7: (a) Microscopic picture of phenolic microbubbles, (b) and the size distribution.
In order to study the effect of the volume fraction of phenolic microbubbles, PUPMB with volume fractions of 10%, 20%, 30%, and 40% phenolic microbubbles were fabricated. Similar to the fabrication of PUMG, phenolic microbubbles were first mixed with Versalink P-1000 before the degassing process. The only difference was in the stirring process. A mechanical stirrer was used instead of a magnetic stirrer, because the highest volume fraction of phenolic microbubbles in this study was 40%, which caused the Versalink+Phenolic Microbubbles mixture to be too viscous for the magnetic stirrer. The mechanical stirrer had a Teflon-coated mixing shaft that could be inserted into the mixing container sealed by a rubber stopper. The degas process was 2 hours before mixing the Isonate 143L with the Versalink P-1000. The PUPMB composites were cured in the environmental chamber for at least 2 weeks before characterization.

The density of PUPMB composites are shown in Fig. 2.8 for the four volume fractions of phenolic microbubbles. When the volume fraction of phenolic microbubbles is higher than 10%, the overall density of PUPMB composite is lower than water.

2.2.2 Scanning electron microscopy on PUPMB

Fig. 2.9 shows the microstructure of the PUPMB composite under the scanning electron microscope (SEM). The fractured surface for SEM was prepared in the same way as PUMG composite. As can be seen on the SEM picture, the shell of phenolic microbubbles is very thin comparing to the diameter of the microbubbles. Different from the PUMG fractured surface (Fig. 2.2), delamination is rarely observed at the boundary between phenolic resin and polyurea matrix. This is due to the similar stiffness, similar thermal expansion coefficients, and similar polarity of phenolic resin.
2.2.3 Dynamic mechanical properties of PUPMB

The dynamic mechanical properties of PUPMB composites (volume fractions of phenolic microbubbles equal 10%, 20%, 30% or 40%) were also tested by DMA single-cantilever bending test.

The DMA results for storage and loss Young’s moduli for various volume fractions of phenolic microbubbles are shown in Fig. 2.10. Only the data tested at 1 Hz are shown in the plot for clarity, and all other frequencies have similar trend. As can be seen from Fig. 2.10, the difference of storage and loss moduli between various volume fractions of phenolic microbubbles is not as prominent as PUMG composites (Fig. 2.4), which means the significant decrease of the material density does not sacrifice much of its viscoelastic properties.
Figure 2.9: Scanning electron microscope (SEM) picture of PUPMB composites.
2.2.4 Discussion on PUPMB

The above results indicate that PUPMB is a lightweight and dissipative material, which have similar viscoelastic properties comparing to polyurea. For designing a dissipative layered composite material that has the same acoustic impedance of water for under water sonar stealth, low impedance layers are needed since the acoustic impedance of water is quite low comparing to most structure materials.

Based on classic solid mechanics theories, the acoustic impedance of a solid is equal to its density times its wave speed, and the wave speed is equal to the square root of the ratio of modulus over density:

\[
Z = \rho c = \rho \sqrt{\frac{M}{\rho}} = \sqrt{\rho M}
\]  

(2.1)

where \(Z\) is the acoustic impedance, \(M\) is the modulus associates with the mode.
of the stress wave propagating in the solid. Eq. 2.1 shows that in order to make a low impedance material, the product of density times stiffness must be low. Foam is such a material, having both low density and low stiffness. However regular polyurea foam collapse easily under pressure. Once it collapses, both its density and wave speed significantly increases and it no longer has the properties of a foam but rather like the matrix material without the voids. But for PUPMB, the phenolic microbubbles do not collapse easily and the acoustic impedance of PUPMB stays invariant when pressure varies between 0-10MPa. This pressure invariant acoustic impedance is ideal for underwater application since pressure changes with the depth under water. Comparing to the phenolic microbubbles, glass microbubbles are also low density hollow spheres. But the stiffness of glass is orders of magnitude higher than phenolic resin, if with the same density, the stiffness of polyurea with glass microbubbles (PUGMB) will be much higher, which results in a higher acoustic impedance than PUPMB. A comparison between phenolic microbubble and one type of glass microbubble is shown in Tab. 2.1. Moreover, phenolic microbubbles bond well with polyurea due to the similarity of the chemical structures and thermal expansion coefficients. Also, they can deform with polyurea matrix. In comparison, glass microbubbles are brittle. Once crushed, they would never regain the strength and therefore affect the overall properties of the composite.

2.3 Summary

In this chapter, two novel polyurea-based composite materials with excellent properties were fabricated and characterized. Both composite materials were fabricated for various volume fractions.
Table 2.1: Properties of phenolic microbubbles comparing to glass microbubbles (K1 from 3M).

<table>
<thead>
<tr>
<th></th>
<th>Glass Microbubble from 3M (K1)</th>
<th>Phenolic Microbubble</th>
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<tr>
<td>Storage Bulk Modulus (GPa)</td>
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<td>5.3</td>
</tr>
<tr>
<td>Storage Shear Modulus (GPa)</td>
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<td>1.37</td>
</tr>
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<td>Poisson’s ratio</td>
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<td>0.38</td>
</tr>
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<td>18.54</td>
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<td>1</td>
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</tbody>
</table>

The first type is polyurea (PU-P1000) with milled glass (PUMG), which has both high storage and loss moduli. 20% volume fraction of milled glass can increase both the storage and loss moduli up to for 4 times comparing to pure polyurea. The other type of composite is polyurea with phenolic microbubbles (PUPMB), which is low-density, dissipative and pressure-invariant for acoustic impedance. 40% volume fraction of phenolic microbubbles can decrease the density of the composite for 30% comparing to pure polyurea, while without sacrificing much of its mechanical properties. It is a robust synthetic foam which has low density and high dissipation. The two types of polyurea composites have been successfully applied for fabricating layered composite material of underwater sonar stealth.

Chapter 2, in part, appears in the paper Dynamic Mechanical Properties of Polyurea-Milled Glass Composites, Part I: DMA and Ultrasonic Wave Experiments, which is in preparation by W. Nantasetphong, Z. Jia, A. V. Amirkhizi, S. Nemat-Nasser. It also appears in part in the conference proceeding Milled Glass Reinforced Polyurea Composites: the Effect of Surface Treatment, in Composite Materials and Joining Technologies for Composites, Volume 7, pp. 35-38. Springer New York, 2013, by Z. Jia, K. Holzworth, and S. Nemat-Nasser. I would like to thank Office of Naval Research for sponsoring this part of research, and I also would like to thank all my
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Chapter 3

Constitutive modeling for polyurea and polyurea composites

Previous chapters discussed the remarkable properties of polyurea and its composites. The aim of this chapter is to develop experimentally-based viscoelastic constitutive models for polyurea and its composites in a format convenient for using in the computational platforms.

In this chapter, polyurea is synthesized using Versalink P-1000 (Air Products and Chemicals, Inc.) and Isonate 143L (Dow Chemicals Co.), and the resultant material is a segmented copolymer which has hard domains dispersed in a soft matrix [13, 57]. The $T_g$ of the soft domain is around $-60^\circ C$, which also was regarded as the $T_g$ of polyurea, and the $T_g$ of the hard domain is above $100 \ ^\circ C$ [57]. Due to the difference of the $T_g$ of the soft and hard segments, in the majority of its application conditions (temperature and frequencies of interest), polyurea is likened to a lightly cross-linked elastomer reinforced by the nano-size hard domains[13], which also serves as chemical and physical cross-link sites.
The wide transition zone of polyurea from rubbery state to glassy state makes the viscoelastic properties of polyurea highly sensitive to the temperature, pressure and strain rate [56, 59, 63]. Throughout the transition zone of polyurea, its stiffness and loss modulus increase drastically from the rubbery state to the glassy state, which makes it an ideal protection material in the high strain rate loading conditions. These properties of polyurea makes its constitutive modeling rather difficult. Comparing to the wide application of polyurea, the number of polyurea material models is limited [25]. The polyurea model in Ref. [4] is a pressure/temperature-sensitive one based on the experimental data of time-domain measurement, where Prony series approximations of relaxation modulus are used to make large scale FEM calculations tractable.

Time-domain measurement is in general less accurate and more difficult to conduct than the dynamic mechanical analysis (DMA). In this chapter, a classical time-temperature superposition (TTS) is used to approximate the mechanical properties of polyurea using the dynamic mechanical analysis data, since directly measurement in such a broad frequency range is not readily available. Recognizing the conditions and the limitations of TTS, care is taken and quality assessments are applied to make sure the use of master curves is not arbitrary. Based on the DMA data, the classical TTS method is applied to develop the frequency-domain master curves which can span more than ten decades on the logarithmic scale.

In order to assess the quality of the master curve, it is compared with ultrasonic wave test data, and is also checked by Kramers-Kronig relations. The frequency-domain master curve is used to calculate the continuous relaxation spectrum, and then the time-domain relaxation modulus is obtained.
Prony series of 4-8 terms are commonly used in the computational platforms. In Ref. [4], 4 Prony terms were used. But small number of Prony terms are not enough to accurately represent the material properties in the entire frequency range of 10 decades or more. Thus, customized Prony series of reduced number of terms are calculated for the specific computational problems to achieve both reliable accuracy and low computational cost.

The same data processing method has been successfully applied for various polyurea and polyurea-based composite systems developed in our lab. These include polyurea with different stoichiometric ratios, polyurea with milled glass inclusions, polyurea with hybrid nano particles and polyurea with phenolic microbubbles. For all these material systems, the stated method has shown great efficiency and consistency in generating the required Young’s modulus viscoelastic properties, which is dominant by shear modulus ($E^* \simeq 3G^*$) for higher temperatures or long relaxation times near rubbery state.

This chapter details this method using the data of pure polyurea and illustrates the final results in terms of two examples of the corresponding composites: polyurea with milled glass (PUMG) and polyurea with phenolic microbubbles (PUPMB). PUMG is an example of polyurea composites with rigid and high-density inclusions and PUPMB is an example with flexible and light-weight inclusions. The master curves of polyurea with various stoichiometric ratios can be found in [30], and the master curves of polyurea with hybrid nano particles will appear in a future publication.

The new contributions of this work are:

1) to develop an automated computational code to efficiently process exper-
imental data of dynamic mechanical analysis to create the Prony series for the viscoelastic properties of polyurea and polyurea composites, suitable for computational platforms.

2) to use the Kramers-Kronig relations to assess the quality of the master curves.

3) to optimize creating the Prony series for the frequency range of interest that minimizes the computational cost.

We note that the presented method is applicable to various similar types of polymers and polymer composites, and is not limited to polyurea.

3.1 Dynamic mechanical analysis

Dynamic mechanical analysis was performed using the TA Instrument Dynamic Mechanical Analyzer 2980 as discussed in Chapter 1. Single-cantilever bending tests were conducted, and DMA data were collected using the corresponding TA data analysis software for various polyurea and polyurea composites.

Multiple samples were tested for each material type. For pure polyurea and PUPMB composites (various volume fractions), we took average of three tests of three samples. Three samples from three different batches for pure polyurea; one sample from one batch and two samples from another batch for PUPMB. For PUMG composites (various volume fractions), one test for each volume fraction was used for this chapter, since we had independent extensive data on the effect of the surface treatment. 8 samples of each volume fraction had been tested, and the result showed the eight tests were the same within experimental error of DMA testing.

The storage and loss moduli DMA data of pure polyurea are shown in Fig.
3.1. Only the data above $T_g + 10^\circ C$ is presented here because relaxation mechanism varies near or below $T_g$. The storage and loss moduli of various volume fractions of PUPMB and PUMG at 1Hz are shown in Fig. 3.2. Pure polyurea and PUPMB.20% are shown as the average storage and loss moduli with the error bars representing the standard deviation. A complete set of PUMG DMA data will be shown in another paper [46].

### 3.2 Master curves development

For most polymers, in the transition zone, increasing temperature has a similar effect on their mechanical properties as decreasing strain rate, and decreasing temperature has a similar effect as increasing strain rate. Thus, instead of testing the material in a wide frequency range, a substitute test can be conducted at a much narrower frequency range but at various temperatures. The material properties tested at various temperatures can be shifted to approximate the wide-frequency response
Traditionally TTS involves both vertical and horizontal shifts for each modulus [16]:

\[
E(\omega_r, T_0) = b(T, T_0)E(\omega, T) \tag{3.1}
\]

\[
\omega_r = a(T, T_0)\omega \tag{3.2}
\]

where \(T_0\) is the reference temperature, \(T\) is the test temperature, \(\omega\) is the test angular frequency, \(\omega_r\) is the reduced angular frequency, \(a(T, T_0)\) is the horizontal shift factor and \(b(T, T_0)\) is the vertical shift factor.

In this work the Young’s modulus of polyurea is directly shifted. It has been discussed in the literature [26, 24], that the bulk and shear response of polymers share the same temperature-frequency response at least at short time scales (around 5 decades below shear relaxation minimum). Some authors suggest that the bulk
and shear transition ranges even span for the same number of decades [50, 17, 5]. For higher temperatures, the Young’s modulus is dominated by the shear modulus \( E^* \simeq 3G^* \).

For the vertical shift, according to [21]:

\[
b(T, T_0) = \frac{T_0 \rho_0}{T \rho}
\] (3.3)

Since the thermal expansion coefficient of polymers is of the order of \( 10^{-4} m/mK \), in the temperature range of interest, the effect of density change is negligible comparing to the effect of the temperature change. Thus in the following calculation we assume \( \rho_0/\rho = 1 \).

The horizontal shift factor \( a(T, T_0) \) can be well fitted by the WLF equation in the material’s transition zone:

\[
\log(a(T, T_0)) = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)}
\] (3.4)

Note that all the temperatures here are in absolute scale.

The storage and loss moduli are shifted independently. The two sets of shift factors, \( \log(a) \), are very close in numbers, which indicates the TTS may be performed in a reasonable way. The average shift factor is taken for developing the final master curves for both storage and loss moduli. The same shift factor may be used in time domain as well.

In this chapter, only the DMA data above \(-50^\circ C\) are used for developing the viscoelastic models, since the classical TTS is usually applied for \( T_g < T < T_g + 100^\circ C \) [77]. \(-50^\circ C\) is sufficiently low for polyurea DMA data to approximate mechanical
properties at frequencies as high as $10^{10}$ Hz.

A good indication that TTS is applicable for this type of material is the Cole-Cole plot, which plots the loss moduli $E''(\omega)$ against $E'(\omega)$, if all the data approximately lie on one line then the horizontal shift of TTS is applicable [27]. Fig. 3.3 (a) shows the Cole-Cole plot of pure polyurea after storage and loss moduli have been vertically shifted by $b(T, T_0)$. As can be seen in the plot, almost all the data points lie on one line, only a small curvature is observed for low temperatures close to $T_g$.

The vertically shifted storage (as is shown in Fig. 3.3 (b)) and loss moduli are then horizontally shifted along the frequency axis to construct master curves. At each temperature $T_i$, data of the five test frequencies are linearly fitted as $y_i = c_i x + d_i$. The increment of the shift factor between two temperature points is defined as:

$$\Delta \log[a(T_i, T_{i+1}, T_0)] = \log[a(T_{i+1}, T_0)] - \log[a(T_i, T_0)]$$

($T_{i+1} = T_i - 3^\circ C$), and it is calculated as:

$$\Delta \log[a(T_i, T_{i+1}, T_0)] = \frac{1}{2c_i c_{i+1}} \cdot |(c_{i+1} - c_i)(c_{i+1}\omega_1 + \omega_m c_i) + (d_{i+1} - d_i)(c_{i+1} + c_i)|$$

which minimizes the horizontal overlapping area between isotherms of neighboring temperatures in Fig. 3.3 (b). Absolute value is taken for the robustness of the code. $[\omega_1, \omega_2, \ldots, \omega_m]$ is the angular frequency table of the DMA test, which equals $2\pi \cdot [1, 2, 5, 10, 20]$ Hz in this study, and $[T_1, T_2, \ldots T_n]$ are the temperature points. $T_1$ is the highest temperature and $T_n$ is the lowest temperature.

The horizontal shift factor therefore is summed up with all the increments:
\[
\log[a(T, T_0)] = \sum_{i=1}^{n_T} \Delta \log[a(T_i, T_{i+1}, T_0)] - \sum_{i=1}^{n_{T_0}} \Delta \log[a(T_i, T_{i+1}, T_0)]
\]  

(3.5)

The first term of Eq. 3.5 is the summation from the highest temperature, and the second term adjusts the \( \log(a) \) to be zero for the reference temperature. \( n_T \) is the index of the temperature array for the temperature \( T \), and \( n_{T_0} \) is the index for the reference temperature \( T_0 \).

The resultant horizontal shift factor and the master curves of pure polyurea are shown in Fig. 3.4 (a) and (b). In Fig. 3.4 (a), the logarithmic scale shift factor was fitted with the WLF model, at a reference temperature \( T_0 = 0^\circ C \), \( C_1 = 32.95 \) and \( C_2 = 253.53K \). As can be seen in Fig. 3.4 (b), both storage and loss moduli form smoothly aligned master curves.

3.3 Master curve quality assessment

3.3.1 Kramers-Kronig relations

The response of a physical system cannot precede the associated excitation in time due to causality. In linear systems, the response function relating the response to excitation may be transformed to the frequency domain. By Titchmarsh’ theorem, this frequency domain function is analytical in the lower-half plane due to the causality considerations, when it is defined in the standard manner \( F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(t)e^{-i\omega t} dt \). The Kramers-Kronig relations are very useful consequences of this analyticity, relating the real and imaginary parts of the response function [43].
Figure 3.3: (a) Cole-Cole plot for pure polyurea. Temperature range from $-50^\circ C$ to $49^\circ C$. Each color represents one temperature point and the temperature increment is $3^\circ C$ between two neighboring lines. (b) DMA storage modulus of pure polyurea vs. angular frequency for temperatures from $-50^\circ C$ to $49^\circ C$, each color line represents $E'$ tested at one temperature point and at five frequencies. The difference between temperature points is $3^\circ C$. The loss modulus plot has similar form.

Figure 3.4: (a) Horizontal shift factor for pure polyurea at reference temperature $T_0 = 0^\circ C$, where $C_1 = 32.95$, and $C_2 = 253.53K$ for a very good WLF fit. (b) Master curves of pure polyurea at reference temperature $T_0 = 0^\circ C$. 
For viscoelastic material systems, the storage and loss moduli are interrelated by
Kramers-Kronig relation as well, as shown in Eq. 3.6 - 3.7 [49, 51, 9]:

\[
E'(\omega) = E_{\omega \rightarrow \infty} + \frac{2}{\pi} \int_{0}^{\infty} \frac{uE''(u)}{\omega^2 - u^2} du
\]  
(3.6)

\[
E''(\omega) = -\frac{2\omega}{\pi} \int_{0}^{\infty} \frac{E'(u)}{\omega^2 - u^2} du
\]  
(3.7)

In Ref. [49], the relations were first derived for the bulk compliance, whereas
they also apply for the elasticity moduli by changing the sign of each right-hand
side. The integrals are understood as the Cauchy principal value and we also assume
all are well-defined and limit all further analysis to viscoelastic solids with finite
instantaneous response.

If the master curves represent the response function of a physical causal ma-
terial system, the storage and loss moduli should follow the relations of Eq. 3.6-3.7.
In order to calculate these integrals, the storage and loss moduli master curves must
be extended to the frequency range of \([0, \infty)\). Using the method in Ref. [61], the
storage modulus is extended as an even function and the loss modulus is extended as
a continuous odd function to ensure the time-domain relaxation modulus \(E(t)\) was
real. The master curves are represented by a set of piece-wise linear functions, then
the integrations could be carried out analytically for each linear segment.

\([\omega_1, \omega_2, ... \omega_n]\) and \([E'_1, E'_2, ... E'_n]\) are the x and y data points of the smoothed
experimental master curves. \([\Omega_0, \Omega_1, ... \Omega_{n+2}]\) and \([\bar{E}'_0, \bar{E}'_1, ... \bar{E}'_{n+2}]\) are the new x and
y data points of the extended master curves in \([0, \infty)\), where \(\bar{E}'_i = \bar{E}'_i + iE''_i\).

The data extension is as follows, and a schematic sketch is shown in the Fig.
Figure 3.5: Piece-wise linear data extension to the \([0, \infty)\). (a) storage modulus master curve is extended as an even function. (b) loss modulus master curve is extended as an odd function.

\[ \Omega_0 = 0, \ \Omega_1 = \frac{\omega_1}{2}, ..., \Omega_n = \frac{\omega_n - \omega_{n-1}}{2}, \ \Omega_{n+1} = \omega_n + \frac{\omega_n - \omega_{n-1}}{2}, \ \Omega_{n+2} = +\infty \]

\[ \overline{E'}_0 = E'_1, \ \overline{E'}_1 = E'_1, ..., \overline{E'}_n = \frac{E'_{n-1} + E'_{n+1}}{2}, \overline{E'}_{n+1} = E'_n, \overline{E'}_{n+2} = E'_n \]

\[ \overline{E''}_0 = 0, \ \overline{E''}_1 = \frac{E''_1}{2}, ..., \overline{E''}_n = \frac{E''_{n-1} + E''_{n+1}}{2}, \overline{E''}_{n+1} = 0, \overline{E''}_{n+2} = 0 \]

Each linear segment of storage modulus is approximated as:

\[ E'(u) = a_i u + b_i, \Omega_i \leq u < \Omega_{i+1}, \ i = 0, 1, ...n + 1. \]

\[ E''(u) = c_i u + d_i, \Omega_i \leq u < \Omega_{i+1}, \ i = 0, 1, ...n + 1. \]
The adjustment on the data extension comparing to Ref. [61] is setting the loss modulus to zero instead of a constant for $E''_{n+1}$ and $E''_{n+2}$, since the intercept of the $n + 1$ segment $d_{n+1}$ must equal zero for the integral (Eq. 3.6) to converge, thus its slope $c_{n+1}$ must equal zero for the loss modulus to be finite at infinite frequency. Note that for the last point of extension in storage modulus, up to 3% adjustment may be applied which is within the experimental error of DMA.

With this modification, the numerical integrations of Eq. 3.6 and 3.7 are (the same as in Ref.[61]):

$$E'(\omega) - E_{\omega \to \infty} = -\frac{2c_0}{\pi} \Omega_1 - \frac{\omega c_0}{\pi} \ln \left| \frac{\Omega_1 - \omega}{\Omega_1 + \omega} \right| - \sum_{i=1}^{n} \left[ \frac{2c_i}{\pi} (\Omega_{i+1} - \Omega_i) \right.$$

$$+ \frac{\omega c_i}{\pi} \ln \left| \frac{(\Omega_{i+1} - \omega)(\Omega_i + \omega)}{(\Omega_{i+1} + \omega)(\Omega_i - \omega)} \right| + \frac{d_i}{2} \ln \left| \frac{\Omega_{i+1}^2 - \omega^2}{\Omega_i^2 - \omega^2} \right] \left. \right]$$

$$E''(\omega) = \frac{b_0}{\pi} \ln \left| \frac{\Omega_1 - \omega}{\Omega_1 + \omega} \right| + \sum_{i=1}^{n} \left[ \frac{\omega a_i}{\pi} \ln \left| \frac{\Omega_{i+1}^2 - \omega^2}{\Omega_i^2 - \omega^2} \right| \right.$$

$$+ \frac{b_i}{\pi} \ln \left| \frac{(\Omega_{i+1} - \omega)(\Omega_i + \omega)}{(\Omega_{i+1} + \omega)(\Omega_i - \omega)} \right| + \frac{b_{n+1}}{\pi} \ln \left| \frac{\Omega_{n+1} + \omega}{\Omega_{n+1} - \omega} \right] \left. \right]$$

By comparing the storage modulus master curve with the one calculated from loss modulus via this technique, and similarly by comparing the loss modulus master curve with the one calculated from storage modulus, the quality of the master curves developed by TTS can be assessed. For pure polyurea, Fig. 3.6 shows the
master curves agree well with Kramers-Kronig relations except for a few points at the two ends of very low and very high frequencies. The difference at the low and high frequencies is due to the lack of information outside the frequency range of the experimental data. Similar results have been observed in other publications [51]. More will be discussed in the discussion section.

The detailed mathematical derivation of this subsection can be found in Appendix B.

### 3.3.2 Verification by ultrasonic wave test

Ultrasonic longitudinal and shear wave tests were conducted at 1MHz to compare with the master curves. Same method was used to measure the longitudinal and shear moduli in Ref. [56], while new test data with less noise are reported here. Two samples of different thicknesses ($d_1$ and $d_2$) were tested and the wave speed and attenuation were measured.

The real and imaginary part of both longitudinal and shear moduli are calculated as:

\[
M' = \frac{\rho c^2 (1 - r^2)}{(1 + r^2)^2} 
\]

\[
M'' = \frac{2\rho c^2 r}{(1 + r^2)^2} 
\]

where $r = \alpha c/\omega$, $\alpha$ is the attenuation, and $c$ is the wave speed.

\[
\alpha = \frac{1}{d} \ln(A_1/A_2) 
\]
$A_1$ is the amplitude of the received signal measured through the thin sample with the thickness $d_1$, and $A_2$ is the amplitude measured through the thick sample with the thickness $d_2$, and $d = d_2 - d_1$. $M'$ and $M''$ represent either longitudinal or shear moduli depending on whether longitudinal or shear waves are considered. The complex Young’s modulus is calculated from the shear modulus $G^*$ and longitudinal modulus $L^*$ as:

$$E^* = \frac{G^*(3L^* - 4G^*)}{L^* - G^*} \quad (3.11)$$

The storage and loss Young’s moduli obtained by ultrasonic wave test are then shifted vertically and also by using the horizontal shift factor $log(a)$ measured from the TTS of DMA data. This ultrasonic master curve is compared with the DMA master curves in Fig. 3.6. Due to the fact that the ultrasonic wave testing at various temperatures is extremely time-consuming, only one set of samples (for longitudinal and shear wave testing) is tested for each material type. As can be seen in Fig. 3.6 and two additional examples for polyurea composites in Fig. 3.10, the ultrasonic storage modulus matches well with the DMA master curves in general, while the ultrasonic loss modulus is higher than the DMA master curves, which is hypothesized to be due to the local resonance in the material [56].

### 3.4 Relaxation spectra

Relaxation spectra represent how all the relaxation mechanisms with different relaxation times contribute to the overall stiffness of the material.
Figure 3.6: Master curve quality check by Kramers-Kronig relations and ultrasonic wave test for pure polyurea at $0^\circ C$.

The relation of relaxation spectrum $H$ and relaxation modulus $E(t)$ is [21]:

$$E(t) = E_e + \int_0^\infty H(\tau)e^{-t/\tau}d\ln\tau$$  \hspace{1cm} (3.12)

here $E_e$ represents the equilibrium modulus when $t \to \infty$. The storage and loss moduli in frequency domain can also be calculated from the relaxation spectrum as:

$$E' = E_e + \int_0^\infty [H(\tau)\omega^2\tau^2/(1 + \omega^2\tau^2)]d\ln\tau$$  \hspace{1cm} (3.13)

$$E'' = \int_0^\infty [H(\tau)\omega\tau/(1 + \omega^2\tau^2)]d\ln\tau$$  \hspace{1cm} (3.14)

The relaxation spectrum may be approximated from the storage and loss moduli though various methods, including continuous relaxation spectrum calculation [65, 22, 21] or numerical calculation for discrete relaxation spectrum [8, 65, 68].

former method includes empirical assumptions and the latter involves relative complex programming to tackle the ill-posed problem of direct fitting from the frequency domain. For simplicity, as one part of our entire computational code, we incorporated the method by [22], and it provides good accuracy for various polyurea and polyurea-based composites. For other more complex material systems, if needed, there are other methods available.

A first estimation of the relaxation spectrum is performed using the storage and loss moduli master curves. The method is summarized in Eq. 3.15-3.19 [22]:

\[
H_A(\tau) \simeq E' \left( \frac{d \log E'}{d \log \omega} \right)_{1/\omega=\tau} \tag{3.15}
\]

\[
H_B(\tau) \simeq E'' \left( 1 - \frac{d \log E''}{d \log \omega} \right)_{1/\omega=\tau} \tag{3.16}
\]

Then the result of the first estimation is used to calculate the adjustment factors \(m_A, m_B, A\) and \(B\).

\[
m_A = \frac{d \log H_A}{d \log \tau}, \quad m_B = \frac{d \log H_B}{d \log \tau} \tag{3.17}
\]

\[
A = \frac{1 + |m_A - 1|}{2\Gamma \left( 2 - \frac{m_A}{2} \right) \Gamma \left( 1 + \frac{m_A}{2} \right)}, \quad -2 \leq m \leq 2
\]

\[
B = \frac{1 + |m_B|}{2\Gamma \left( \frac{3}{2} - \frac{m_B}{2} \right) \Gamma \left( \frac{3}{2} + \frac{m_B}{2} \right)}, \quad -1 \leq m \leq 3
\]

where \(\Gamma\) represents the Gamma Function \(\Gamma(t) = \int_0^\infty x^{t-1}e^{-x}dx\). With these
adjustment factors, the second approximation of $H$ is calculated as:

$$H_A(\tau) = AE' \left( 1 - \left| \frac{d \log E'}{d \log \omega} - 1 \right| \right)_{1/\omega=\tau}$$

$$H_B(\tau) = BE'' \left( 1 - \left| \frac{d \log E''}{d \log \omega} \right| \right)_{1/\omega=\tau}$$

If the storage and loss moduli master curves have good inherent consistency, Eq. 3.18 and 3.19 should give the same or similar relaxation spectra. A representative relaxation spectra for pure polyurea at 0°C are shown in Fig. 3.7. The blue square curve is the relaxation spectrum calculated from storage modulus $E'$, and the green star curve is the relaxation spectrum calculated from loss modulus $E''$. Besides Kramers-Kronig relations and the ultrasonic test verification, the similarity of the two relaxation spectra is another piece of evidence that the master curves of storage and loss moduli developed from TTS have good inherent consistency.

In the relaxation spectrum calculations, all the derivatives are calculated by taking the slope of the linear fitting of the neighboring 11 data points (5 points on the left and 5 points on the right).

### 3.5 Time-domain Master Curves

The discrete form of Eq. 3.12 is the Prony series

$$E(t) = E_e + \sum_{i=1}^{n} E_i e^{-t/\tau_i}$$
Figure 3.7: Relaxation spectra of pure polyurea at 0°C, calculated from the master curves of $E'$ and $E''$.

where $E_i$ and $\tau_i$ are the stiffness and relaxation time of the $i^{th}$ Maxwell dashpot-spring element [21]. In the frequency domain it can be easily written as:

$$E'(\omega) = E_e + \sum_{i=1}^{n} E_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}$$  \hspace{1cm} (3.21)$$

$$E''(\omega) = \sum_{i=1}^{n} E_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}$$  \hspace{1cm} (3.22)$$

If sufficient number of terms are used, Eq. 3.21-3.22 should be able to represent the master curve with good accuracy. By using the same set of high-resolution $E_i$ and $\tau_i$, the relaxation modulus Eq. 3.20 can be obtained. For the best accuracy of the relaxation modulus, the maximum number of terms is used, such that the number of Prony terms is equal to the number of data points in the frequency-domain master curve.

Starting with the relaxation spectrum data, the magnitude of each Prony term
is approximated as:

$$E_i = H(\tau_i)(ln\tau_{i+1} - ln\tau_i)|_{\omega_i=1/\tau_i} \quad (3.23)$$

where $\tau_i$ and $H(\tau_i)$ are the x and y axes of the $i^{th}$ data point of the relaxation spectrum shown in Fig. 3.7, and assuming $\tau_{i+2}$ exists and $ln\tau_{i+2} - ln\tau_{i+1} = ln\tau_{i+1} - ln\tau_i$.

The equilibrium storage modulus $E_e$ is calculated as:

$$E_e = \frac{1}{n} \sum_{i=1}^{n} \left[ E'(\omega_i) - \sum_{j=1}^{n} E_j \frac{\omega_i^2 \tau_j^2}{1 + \omega_i^2 \tau_j^2} \right] \quad (3.24)$$

The master curves plotted by the high-resolution Prony series (Eq. 3.21-3.22, with maximum n) lie on top of the master curves developed from TTS. Note that although $E'$ values are used directly, the major portion of data is extracted from the relaxation spectrum $H$ which was just shown to be the same function regardless of whether one starts from $E'$ or $E''$ master curves.

This section further insures that the relaxation modulus can accurately represent information of the frequency domain master curves at all frequencies except for the two ends near 0 and infinite frequencies, where experimental information is deficient.

Time-domain Young’s modulus of polyurea can also be well represented in this power-law form [4]:

$$E(t,T) = \frac{T}{T_0} \left( E_{t\to\infty} + \Delta E \left( \frac{t}{a(T)} \right)^{-\theta} \right) \quad (3.25)$$

The unit of time $t$ is in seconds. At the reference temperature, Eq. 3.25
becomes the time-domain master curve:

$$E(t, T = T_0) = E_{t\to\infty} + \Delta E t^{-\theta}$$  \hspace{1cm} (3.26)

For pure polyurea at reference temperature $0^\circ C$, the three parameters are fitted as:

$$E_{t\to\infty} = 78.46 MPa$$

$$\Delta E = 32.45 MPa$$

$$\theta = 0.1396$$

As can be seen in Fig. 3.8, this power-law expression (Eq. 3.26) can represent the time-domain master curve very well. The only shortcoming of this representation is that for explicit finite element calculations there is no straightforward algorithm for incremental time integration.

### 3.6 Customized reduced-term Prony series

However, more than 100 Prony terms make this high-resolution Prony series hard to use on the actual computational platforms. Thus a further step is taken to reduce the number of Prony terms while maintaining the usefulness of the Prony series. We call this step a customizing procedure, in other words, we create a cus-
Figure 3.8: Power law compared with high-resolution Prony series for pure polyurea.

tomized Prony series suitable for a limited frequency range of interest for the specific computational problem to obtain both good accuracy and low computational cost.

Usually Prony series of 4-8 terms can be conveniently applied in computational platforms. This reduced term Prony series can be calculated by applying the least square fitting using the time domain relaxation modulus.

Assuming the frequency range of interest for the computational problem is \( \omega_{\text{min}} < \omega < \omega_{\text{max}} \), the corresponding time range is \( t_{\text{min}} = \frac{1}{\omega_{\text{max}}} < t < \frac{1}{\omega_{\text{min}}} = t_{\text{max}} \).

The data points of time within this range are \([t_1, t_2, ..., t_m]\), and the relaxation times \([\tau_1, \tau_2, ..., \tau_p]\) can be assigned as equally spaced in the logarithmic scale within this time range. Given the relatively flat spectrum for these polymers, the equidistant choice of discrete times is a reasonable choice. Then the optimized amplitude of each Prony term can be calculated as:
Figure 3.9: (a) Master curves and Prony series approximation at $10^2 - 10^8$ Hz for pure polyurea at $0^\circ$C (b) Relaxation modulus and Prony series approximation at $10^2 - 10^8$ Hz for pure polyurea at $0^\circ$C

\[
\begin{bmatrix}
E_0 \\
E_1 \\
\vdots \\
E_p
\end{bmatrix} = (A^T A)^{-1} A^T
\begin{bmatrix}
E(t_1) \\
E(t_2) \\
\vdots \\
E(t_m)
\end{bmatrix}, \text{ where } A =
\begin{bmatrix}
1 & e^{-t_1/\tau_1} & \ldots & e^{-t_1/\tau_p} \\
1 & e^{-t_2/\tau_1} & \ldots & e^{-t_2/\tau_p} \\
\vdots & \vdots & \ddots & \vdots \\
1 & e^{-t_m/\tau_1} & \ldots & e^{-t_m/\tau_p}
\end{bmatrix}_{m \times p}
\]

An example of 8-term Prony series is shown in Fig. 3.9 (a) and (b) for the frequency range from $10^2$ to $10^8$ Hz. The parameters of this 8-term Prony series are listed in Table 3.1.

3.7 Example results for polyurea based composites

The same method of TTS has been applied for many polyurea-based composite systems. Two examples are polyurea with milled glass (PUMG), and polyurea with
Table 3.1: 8-term Prony series to approximate the pure polyurea properties within the range of $10^2 - 10^8$ Hz at $0^\circ C$.

<table>
<thead>
<tr>
<th>$E_i$ [MPa]</th>
<th>$\tau_i$ [s]</th>
<th>$\tau_e$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_e$</td>
<td>126.48</td>
<td>$\infty$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>194.63</td>
<td>$5.05E-09$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>123.71</td>
<td>$7.00E-08$</td>
</tr>
<tr>
<td>$E_3$</td>
<td>82.60</td>
<td>$8.40E-07$</td>
</tr>
<tr>
<td>$E_4$</td>
<td>51.90</td>
<td>$8.21E-06$</td>
</tr>
<tr>
<td>$E_5$</td>
<td>37.84</td>
<td>$6.82E-05$</td>
</tr>
<tr>
<td>$E_6$</td>
<td>28.04</td>
<td>$5.10E-04$</td>
</tr>
<tr>
<td>$E_7$</td>
<td>16.86</td>
<td>$3.46E-03$</td>
</tr>
<tr>
<td>$E_8$</td>
<td>21.72</td>
<td>$2.14E-02$</td>
</tr>
</tbody>
</table>

phenolic microbubbles (PUPMB). The master curves of TTS are compared with both ultrasonic data and are checked by the Kramers-Kronig relations, as shown in Fig 3.10. Similar to what is observed for pure polyurea in Fig. 3.6, higher loss modulus of ultrasonic measurement and Kramers-Kronig relation edge effect are observed. The relaxation moduli of pure polyurea, PUMG and PUPMB are shown in Fig. 3.11.

The power law (Eq. 3.26) parameters for pure polyurea, PUMG and PUPMB are summarized in Table 3.2. These power law parameters can be used to plot the relaxation moduli (shown in Fig. 3.11) for calculating the optimized parameters of the Prony series.

The WLF parameters $C_1$ and $C_2$ for pure polyurea, PUMG, and PUPMB are summarized in Table 3.3.

### 3.8 8-term Prony series for polyurea composites

8-term Prony series for PUMG (volume fraction 10%, 15%, 20%) and PUPMB (volume fraction 10%, 20%, 30%, 40%) are also calculated for the frequency range of $10^2 - 10^8$ Hz at $0^\circ C$. (Tab. 3.4-3.10)
Figure 3.10: (a) Master curve quality check by Kramers-Kronig relations and ultrasonic wave test for polyurea with 20% volume fraction of milled glass at 0 °C. (b) Master curve quality check by Kramers-Kronig relations and ultrasonic wave test for polyurea with 20% volume fraction of phenolic microbubbles at 0 °C.

Figure 3.11: Relaxation modulus $E(t)$ of PUMG and PUPMB composites at varying volume fractions. All curves at reference temperature $T_0 = 0^\circ C$.
Table 3.2: Power law parameters for pure polyurea, PUMG and PUPMB for reference temperature at 0\(^\circ\)C.

<table>
<thead>
<tr>
<th>Material Name</th>
<th>(E_t\rightarrow\infty) [MPa]</th>
<th>(\Delta E) [MPa]</th>
<th>(\theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PU</td>
<td>78.46</td>
<td>32.45</td>
<td>0.1396</td>
</tr>
<tr>
<td>PUMG_10%</td>
<td>156.11</td>
<td>95.25</td>
<td>0.1167</td>
</tr>
<tr>
<td>PUMG_15%</td>
<td>197.86</td>
<td>135.46</td>
<td>0.1088</td>
</tr>
<tr>
<td>PUMG_20%</td>
<td>283.14</td>
<td>239.04</td>
<td>0.0949</td>
</tr>
<tr>
<td>PUPMB_10%</td>
<td>89.74</td>
<td>34.77</td>
<td>0.1327</td>
</tr>
<tr>
<td>PUPMB_20%</td>
<td>95.63</td>
<td>39.42</td>
<td>0.1247</td>
</tr>
<tr>
<td>PUPMB_30%</td>
<td>102.93</td>
<td>43.02</td>
<td>0.1184</td>
</tr>
<tr>
<td>PUPMB_40%</td>
<td>106.63</td>
<td>54.89</td>
<td>0.1059</td>
</tr>
</tbody>
</table>

Table 3.3: WLF parameters \(C_1\) and \(C_2\) for pure polyurea, PUMG and PUPMB for reference temperature at 0\(^\circ\)C.

<table>
<thead>
<tr>
<th>Material Name</th>
<th>(C_1)</th>
<th>(C_2[K])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PU</td>
<td>32.95</td>
<td>253.53</td>
</tr>
<tr>
<td>PUMG_10%</td>
<td>29.39</td>
<td>227.15</td>
</tr>
<tr>
<td>PUMG_15%</td>
<td>31.09</td>
<td>237.015</td>
</tr>
<tr>
<td>PUMG_20%</td>
<td>44.98</td>
<td>317.83</td>
</tr>
<tr>
<td>PUPMB_10%</td>
<td>33.89</td>
<td>260.31</td>
</tr>
<tr>
<td>PUPMB_20%</td>
<td>36.15</td>
<td>272.42</td>
</tr>
<tr>
<td>PUPMB_30%</td>
<td>39.60</td>
<td>294.95</td>
</tr>
<tr>
<td>PUPMB_40%</td>
<td>41.42</td>
<td>295.88</td>
</tr>
</tbody>
</table>

Table 3.4: 8-term Prony series of PUMG_10% for the range of \(10^2 \text{ – } 10^8\)Hz at 0\(^\circ\)C.

<table>
<thead>
<tr>
<th>(E_i) [MPa]</th>
<th>(\tau_i) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_e) 283.70</td>
<td>(\tau_e) (\infty)</td>
</tr>
<tr>
<td>(E_1) 275.74</td>
<td>(\tau_1) 5.31E-09</td>
</tr>
<tr>
<td>(E_2) 203.28</td>
<td>(\tau_2) 6.89E-08</td>
</tr>
<tr>
<td>(E_3) 146.60</td>
<td>(\tau_3) 7.81E-07</td>
</tr>
<tr>
<td>(E_4) 104.97</td>
<td>(\tau_4) 7.81E-06</td>
</tr>
<tr>
<td>(E_5) 79.78</td>
<td>(\tau_5) 7.78E-05</td>
</tr>
<tr>
<td>(E_6) 57.63</td>
<td>(\tau_6) 6.43E-04</td>
</tr>
<tr>
<td>(E_7) 34.98</td>
<td>(\tau_7) 4.28E-03</td>
</tr>
<tr>
<td>(E_8) 46.63</td>
<td>(\tau_8) 2.54E-02</td>
</tr>
</tbody>
</table>
Table 3.5: 8-term Prony series of PUMG.15% for the range of 10^2 – 10^8Hz at 0°C.

<table>
<thead>
<tr>
<th>$E_i$ [MPa]</th>
<th>$\tau_i$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_e$</td>
<td>$\tau_e$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>$\tau_1$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>$\tau_2$</td>
</tr>
<tr>
<td>$E_3$</td>
<td>$\tau_3$</td>
</tr>
<tr>
<td>$E_4$</td>
<td>$\tau_4$</td>
</tr>
<tr>
<td>$E_5$</td>
<td>$\tau_5$</td>
</tr>
<tr>
<td>$E_6$</td>
<td>$\tau_6$</td>
</tr>
<tr>
<td>$E_7$</td>
<td>$\tau_7$</td>
</tr>
<tr>
<td>$E_8$</td>
<td>$\tau_8$</td>
</tr>
</tbody>
</table>

Table 3.6: 8-term Prony series of PUMG.20% for the range of 10^2 – 10^8Hz at 0°C.

<table>
<thead>
<tr>
<th>$E_i$ [MPa]</th>
<th>$\tau_i$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_e$</td>
<td>$\tau_e$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>$\tau_1$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>$\tau_2$</td>
</tr>
<tr>
<td>$E_3$</td>
<td>$\tau_3$</td>
</tr>
<tr>
<td>$E_4$</td>
<td>$\tau_4$</td>
</tr>
<tr>
<td>$E_5$</td>
<td>$\tau_5$</td>
</tr>
<tr>
<td>$E_6$</td>
<td>$\tau_6$</td>
</tr>
<tr>
<td>$E_7$</td>
<td>$\tau_7$</td>
</tr>
<tr>
<td>$E_8$</td>
<td>$\tau_8$</td>
</tr>
</tbody>
</table>

Table 3.7: 8-term Prony series of the PUPMB.10% for the range of 10^2 – 10^8Hz at 0°C.

<table>
<thead>
<tr>
<th>$E_i$ [MPa]</th>
<th>$\tau_i$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_e$</td>
<td>$\tau_e$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>$\tau_1$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>$\tau_2$</td>
</tr>
<tr>
<td>$E_3$</td>
<td>$\tau_3$</td>
</tr>
<tr>
<td>$E_4$</td>
<td>$\tau_4$</td>
</tr>
<tr>
<td>$E_5$</td>
<td>$\tau_5$</td>
</tr>
<tr>
<td>$E_6$</td>
<td>$\tau_6$</td>
</tr>
<tr>
<td>$E_7$</td>
<td>$\tau_7$</td>
</tr>
<tr>
<td>$E_8$</td>
<td>$\tau_8$</td>
</tr>
</tbody>
</table>
Table 3.8: 8-term Prony series to approximate the PUPMB.20% properties within the range of $10^2 - 10^8$ Hz at 0°C.

<table>
<thead>
<tr>
<th>$E_i$ [MPa]</th>
<th>$\tau_i$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_e$</td>
<td>151.55</td>
<td>$\tau_e$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>153.83</td>
<td>$\tau_1$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>96.97</td>
<td>$\tau_2$</td>
</tr>
<tr>
<td>$E_3$</td>
<td>71.22</td>
<td>$\tau_3$</td>
</tr>
<tr>
<td>$E_4$</td>
<td>48.58</td>
<td>$\tau_4$</td>
</tr>
<tr>
<td>$E_5$</td>
<td>36.89</td>
<td>$\tau_5$</td>
</tr>
<tr>
<td>$E_6$</td>
<td>26.89</td>
<td>$\tau_6$</td>
</tr>
<tr>
<td>$E_7$</td>
<td>16.03</td>
<td>$\tau_7$</td>
</tr>
<tr>
<td>$E_8$</td>
<td>20.81</td>
<td>$\tau_8$</td>
</tr>
</tbody>
</table>

Table 3.9: 8-term Prony series to approximate the PUPMB.30% properties within the range of $10^2 - 10^8$ Hz at 0°C.

<table>
<thead>
<tr>
<th>$E_i$ [MPa]</th>
<th>$\tau_i$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_e$</td>
<td>163.04</td>
<td>$\tau_e$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>140.24</td>
<td>$\tau_1$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>90.57</td>
<td>$\tau_2$</td>
</tr>
<tr>
<td>$E_3$</td>
<td>66.75</td>
<td>$\tau_3$</td>
</tr>
<tr>
<td>$E_4$</td>
<td>46.65</td>
<td>$\tau_4$</td>
</tr>
<tr>
<td>$E_5$</td>
<td>35.55</td>
<td>$\tau_5$</td>
</tr>
<tr>
<td>$E_6$</td>
<td>26.70</td>
<td>$\tau_6$</td>
</tr>
<tr>
<td>$E_7$</td>
<td>16.35</td>
<td>$\tau_7$</td>
</tr>
<tr>
<td>$E_8$</td>
<td>21.05</td>
<td>$\tau_8$</td>
</tr>
</tbody>
</table>

Table 3.10: 8-term Prony series to approximate the PUPMB.40% properties within the range of $10^2 - 10^8$ Hz at 0°C.

<table>
<thead>
<tr>
<th>$E_i$ [MPa]</th>
<th>$\tau_i$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_e$</td>
<td>178.90</td>
<td>$\tau_e$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>125.30</td>
<td>$\tau_1$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>92.52</td>
<td>$\tau_2$</td>
</tr>
<tr>
<td>$E_3$</td>
<td>67.13</td>
<td>$\tau_3$</td>
</tr>
<tr>
<td>$E_4$</td>
<td>47.23</td>
<td>$\tau_4$</td>
</tr>
<tr>
<td>$E_5$</td>
<td>34.15</td>
<td>$\tau_5$</td>
</tr>
<tr>
<td>$E_6$</td>
<td>27.86</td>
<td>$\tau_6$</td>
</tr>
<tr>
<td>$E_7$</td>
<td>19.62</td>
<td>$\tau_7$</td>
</tr>
<tr>
<td>$E_8$</td>
<td>22.64</td>
<td>$\tau_8$</td>
</tr>
</tbody>
</table>
3.9 Summary and discussion

This chapter develops a consistent method to obtain Prony series of polyurea and polyurea-based composites using the DMA test data.

A flowchart of the method is shown in Fig. 3.12. The four inputs of this method are the DMA test data, reference temperature \( T_0 \), frequency range of interest and the number of Prony terms. We have developed a computer code that automatically processes the data including the master curve development by time-temperature superposition, creates graphs for quality assessment of the master curves, and finally performs relaxation spectra calculation, time-domain relaxation modulus calculation, and the reduced-term Prony series calculation. This method gives an efficient constitutive model, which gives good accuracy while maintaining the low computational cost.
After the data processing platform is constructed, the most effort for getting a shear viscoelastic constitutive model remains in the sample fabrication and DMA test. The data processing takes negligible time on a regular PC, and it gives the reduced-term Prony series that can be directly used in finite element explicit codes. Other necessary information can also be acquired through the data processing, including the shift factor $\log(a)$, which represents the temperature effect on the material relaxation mechanism, and has to be incorporated to consider the temperature change in some adiabatic deformation [4].

Regarding the applicability of TTS to polyurea and polymer composites, different opinions exit [60]. Due to the phase separation in the polyurea and the heterogeneity in the microstructure of polymer composites, not all components in the material share the same set of relaxation mechanisms, and that is the main reason to question the applicability of TTS. However, this does not completely exclude TTS as a useful empirical estimation for copolymers like polyurea when substitute tests are not easily available.

The hard domains of polyurea are nano-meter size [13], and the $T_g$ of the hard domain is significantly higher than the soft domain [57], we expect most of the relaxation happens in the soft domain for most of the frequencies, while for the extremely high frequency above $10^9$ Hz, some energy may go into the local resonance due to the existence of the hard domains. For most applications, $10^9$ Hz is high enough. The master curves may still be a good starting point for those extremely high strain rate problem to use as a computational guidance.

For polyurea composites, the reliable frequency range of the master curves needs to be estimated based on the size, mass and distribution of the inclusions.
For the composites examples of PUMG and PUPMB, due to the micrometer size inclusions, the master curves are more reliable in the lower frequency range. For example, their master curves can be used for acoustic problems.

The verification by the Kramers-Kronig relations shows the master curves of storage and loss moduli are interrelated and are representing a causal physical system. The discrepancy at the two frequency ends of the loss modulus does not mean the master curves are not reliable at low and high frequencies. It is actually related with how the experimental data are extrapolated to $\omega \in [0, \infty)$. By changing the way of data extension, i.e., adjusting the value of the $E'(\omega = \infty)$, and moving the positions of $\Omega_1$ and $\Omega_{n+1}$ to be closer to the physical case, or possibly changing the piece-wise linear extrapolation to higher order, the discrepancy of the calculated loss modulus may be reduced.

The method discussed in this paper can also be applied for other polymers or for bulk modulus. The temperature range of the DMA test needs to be determined for other polymers and the reference temperature needs to lie in the temperature range of the TTS. Experience shows the Young’s moduli tested by single-cantilever bending and thin-film tension tests are almost the same for polyurea on TA2980, as long as appropriate tests are conducted within the machine’s test range. If the available sample size is small, a thin-film tension test can replace the single-cantilever bending test.


I would like to thank Office of Naval Research for sponsoring this part of re-
search, and I also want to thank all of my coauthors for their efforts and contributions in this project.
Chapter 4

Interface study for polyurea composites

Interface is an important element for polyurea composites. There are various types of interfaces between polyurea and another material, such as ceramic, glass, metal and polymers. From the point of view of energy management, more energy can be dissipated in a composite material by the enhanced shearing at the boundaries of the filler materials or through the debonding at the interfaces between the matrix and the inclusions [70, 45]. Stronger bonding at the interface does not necessarily increase energy dissipation in the composite material. An inferior adhesion sometimes absorbs more energy during the impacts [45].

Knowledge about the interface is essential for the design and fabrication of polyurea composite materials for both static and dynamic applications. This chapter studies the modifications, characterization and modeling of the interfaces for two types of polyurea interfaces, which are polyurea-glass interface and polyurea-metal interface. Polyurea-glass and polyurea-metal are two types of interfaces that are
common for polyurea application. The type of polyurea used in this chapter is PU-P1000.

4.1 Polyurea-glass interface

In this section, modification, characterization and modeling of polyurea-glass interfaces are discussed. Glass is a widely used filler material, which is also cost-effective and available in various shapes and sizes. Some of the common glass filler materials are glass fibers, milled glass, glass beads or hollow glass spheres. The knowledge obtained from this part of study enables us to control the interface adhesion between polyurea and glass from weak to strong, to characterize the tensile and shear properties of the modified interfaces, and to model the shear cohesive law for the covalently-bonded PU-glass interface.

4.1.1 Tailoring the polyurea-glass interface

Silane surface treatment can be applied on the glass surface to graft functional groups on the glass surface. Various functional groups grafted on the glass surface have various chemical functionality, thus can interact with polyurea to create various bonding strengths.

Hydroxyl groups on the glass surface are essential for the silane surface treatment. They are “anchor points” for grafting organosilane molecules [54, 44]. In other words, various organosilane surface treatment reagents need to bond with the hydroxyl sites to graft functional groups onto the glass substrate. Hydroxyl sites not only exist on the surface of the glass, they are also found on the surfaces of silica or metal oxides [12]. The same chemistry of surface treatment that applies for glass
Table 4.1: Surface treatment reagents and their corresponding functional groups and the types of bonding with polyurea.

<table>
<thead>
<tr>
<th>Organosilane Chemical Name</th>
<th>Functional Group</th>
<th>Bonding with Polyurea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethoxy(octyl)silane</td>
<td>Aliphatic chain</td>
<td>Van de Waals’ force</td>
</tr>
<tr>
<td>1-[3-(trimethoxysilyl)propyl]urea</td>
<td>Urea</td>
<td>Hydrogen bond</td>
</tr>
<tr>
<td>(3-aminopropyl)trimethoxysilane</td>
<td>Amine</td>
<td>Covalent bond</td>
</tr>
</tbody>
</table>

surface is also applicable for other surfaces that have hydroxyl sites.

In order to modify the bonding strength of the glass-polyurea interface, three types of silanes are chosen. The three types of surface treatment reagents and their functional groups are listed in Tab. 4.1. For briefness, the three types of surface treatments are referred to as aliphatic, urea and amine surface treatment respectively.

The three types of silanes have similar molecular structures but varied functional groups to interact with polyurea. They bond with glass through the same chemical reaction [18]. After these silanes are grafted on the glass surface, the functional groups on top of the silane molecules determine the types of bonding with polyurea. The aliphatic chain on trimethoxy(octyl)silane bonds with polyurea through Van de Waals force; the urea group on 1-[3-(trimethoxysilyl)propyl]urea forms hydrogen bonds with the urea groups in the polyurea; the amine group on (3-aminopropyl)trimethoxysilane has the same functionality as the amine group in Versalink, thus can react with Isonate 143L to form covalent bond with polyurea.

The three types of silanes listed in Tab. 4.1 were purchased from Sigma-Aldrich. The same procedure was followed for three types of surface treatment.

For micro-glass, such as milled glass, the surface treatment procedure is as follows:

1. Create “piranha solution” using 3:1 volume ratio of sulfuric acid to hydrogen peroxide (98% $H_2SO_4$: 30% $H_2O_2 = 3:1$). This solution is extremely corrosive and
can become very hot when mixed. It needs to be handled with care.

2. Put a medium frit on top of the vacuum flask.

3. Soak milled glass in the boiling piranha solution and agitate for 10 minutes. Piranha solution removes all the organic compounds on the glass surface and exposes the hydroxyl sites on the glass surface.

4. Pour the piranha solution with the milled glass into the medium frit.

5. Pull vacuum on the vacuum flask to extract the milled glass.

6. Use milli-Q water to rinse milled glass in the frit for multiple times and filter until the acidity is removed.

7. Prepare solvent for silanes: 95% ethanol+5% water.

8. Prepare silane solution. Add accurate amount of silane with stirring to prepare a 0.1mol/L concentration. Based on the density of hydroxyl sites on the glass surface [81, 78], the concentration of the silane solution is estimated to ensure all the hydroxyl sites can be covered.

9. Keep stirring the silane solution for 5 minutes to allow hydrolysis and silanol formation.

10. Add silane solution to the milled glass and agitate for 2 minutes.

11. Pull the vacuum and filter out the milled glass.

12. Rinse with milled glass with ethanol in the frit twice to remove the excess silane.

13. Filter out the milled glass, and transfer the milled glass onto a flat glassware.

14. Put the surface-treated milled glass in a vacuum oven at 110 °C overnight to cure the layer of surface treatment.
• For a larger piece of glass instead of micro-glass, frit is not needed, and the surface treatment layer can be cured in a regular oven at 110°C for one hour. The purpose of vacuum during the drying process is to prevent the micro-glass from agglomerating.

• A control group is also created. The control group is only washed by the “piranha” solution, rinsed by milli-Q water and dried in the vacuum oven at 110°C.

It should be noted that in order to obtain comparable results, reaction time, temperature and concentration need to be controlled during the surface treatment, since silanization is influenced by the reaction conditions such as temperature and solution concentration [32, 75]. In this study, all the surface treatment conditions are kept consistent for the three types of silane surface treatments.

Fig. 4.1 is the schematic diagram showing how each type of surface treatment grafts molecules on the glass surface. The control group is labeled as “After Piranha” in Fig. 4.1. Similar to the urea surface treatment, the hydroxyl sites (-OH) on the glass surface can also create hydrogen bonds with the urea linkages in the polyurea.

In this chapter, the effectiveness of the surface treatment is studied in multiple methods focusing on the mechanical properties of the polyurea-glass interface. However, there are other methods available to examine the effectiveness of surface treatment, such as infrared spectroscopy or atomic-force microscopy [76, 32]. Infrared spectroscopy can detect the attachment of certain functional groups on the glass surface, and atomic-force microscopy can image the surface of the polymerized silane layer on the glass.

Three forms of glass were surface treated. The first form of glass was the
milled glass, which was used as the filler material for making polyurea with milled
glass (PUMG) composites. The second type was microscopic glass slide, which was
cut into squares and used for the pull-up tests to characterize the tensile strength
of the polyurea-glass interface. The third type of glass was the long E-glass fiber,
which was used to fabricate single-fiber fragmentation test samples for characterizing
the shear property of the polyurea-glass interface. After the samples were fabricated
and cured for two weeks, the effect of the surface treatment was studied from various
perspectives:

1) Contact angle measurement on the surface-treated glass plates

2) Observation of the fractured surface of PUMG under scanning electron
microscope (SEM)

3) Dynamic mechanical analysis (DMA) on the surface-treated PUMG com-
posites.
4) Polyurea pull-up tests for estimating the tensile strengths of the polyurea-glass interfaces.

5) Single-fiber fragmentation tests for estimating the shear strengths of the polyurea-glass interfaces.

4.1.2 Contact angle measurements for the surface-treated glass plates

After the microscopic glass slides were surface-treated, the static water contact angles were measured on the surface-treated glass plates. 0.2ml of deionized water was carefully added on the top of the surface-treated glass plates, and the pictures of the contact angle were taken sideways, as shown in Fig. 4.2. An averaging of 10 measurements was taken to measure the contact angle for each surface treatment.

The measured average contact angles are listed in Table 4.2. This result shows that the contact angle is more influenced by the chain length and the whole molecular structure of the organosilane, and is less dependent on the polarity of the end functional group, which is in consistent with the observation reported in the literature [34, 42]. These studies show that contact angle is not only determined by the polarity of the functional groups of the silanes alone, it is also affected by the substrate and is more dominated by the chain length of the graphed silanes and the size of the silane molecules. The glass plates treated by the three types of silanes have the same contact angle even though they have very different functional groups, because the three types of surface treatment reagents have similar molecular sizes and chain lengths. The comparison between the control group and urea surface treatment shows that even when the functional groups on the glass surface have similar polarity, the
Figure 4.2: Contact angle observation of the surface-treated microscopic glass plates.

Table 4.2: Contact angle measurements for various types of surface treatment.

<table>
<thead>
<tr>
<th>Surface Treatment Type</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>After Piranha</td>
<td>36°</td>
</tr>
<tr>
<td>Aliphatic</td>
<td>60°</td>
</tr>
<tr>
<td>Urea</td>
<td>60°</td>
</tr>
<tr>
<td>Amine</td>
<td>60°</td>
</tr>
</tbody>
</table>

contact angles of water droplets can be very different if the chain lengths or molecular structures on the glass plates are different.

The measured contact angle of (3-aminopropyl)trimethoxysilane (or APTES) in Tab. 4.2 is very close to the reported contact angle of APTES in [34], which is $58.4° \pm 1.7°$.

4.1.3 Fractured surfaces of PUMG under scanning electron microscope

The surface-treated milled glass and the control group (as shown in Fig. 4.1) were added as the filler materials into polyurea matrix to fabricate PUMG composites following the fabrication procedure discussed in Chapter 2. After the composite samples were fully cured, the fractured surfaces of the composites were prepared by fracturing PUMG at a low temperature that was equilibrated with liquid nitrogen. Scanning electron microscope (SEM) pictures were taken for the four fractured sur-
faces.

The SEM pictures of the control group and the three types of surface treatments are shown in Fig. 4.3. In consistent with the prediction by the chemical interaction between the grafted functional group and polyurea, the aliphatic surface-treated sample has the weakest bonding strength at the interface, which is bonded by Van de Waals force; the control group and the urea surface-treated sample have the intermediate bonding strength through the hydrogen bonds with polyurea; and the amine surface-treated sample has the strongest bonding strength by covalent bonds.

In Fig. 4.3, the aliphatic-treated sample has separation at the interface and the separation also propagates along the interface into the composite; the control group and the urea surface-treated samples both have separation at the polyurea-glass interface because the protruding milled glass has clean surfaces, but the debonding does not propagate into the polyurea composites under the same fracture condition; the amine-treated interface has the strongest bonding because the failure happens in the polyurea but not at the interface and the protruding milled glass is covered with polyurea.

### 4.1.4 Dynamic mechanical analysis of PUMG composites

In order to study the effect of the interface bonding strength on the viscoelastic properties of PUMG composites, dynamic mechanical analysis single cantilever tests were conducted on PUMG composites for the four types of surface treatment (three types of organosilanes surface treatments and one control group). The DMA tests were conducted from $-80^\circ C$ to $50^\circ C$, and the test frequencies were 1, 2, 5, 10, 20 Hz. The oscillation amplitude of the movable end of the cantilever was 15 $\mu m$. 
Figure 4.3: Fractured surfaces of polyurea with milled glass composites observed under SEM. “After Piranha” represents the control group, in which milled glass was only washed by piranha solution and rinsed by water.

The span between two cantilever was 17.5 mm, and the nominal sample size was $3mm \times 10mm \times 30mm$.

The storage and loss Young’s modulus tested at 1 Hz are shown in Fig. 4.4, and the other frequencies all show similar trend. No obvious difference is observed for various types of surface treatments even though the interface bonding strengths are very different between various surface treatments as indicated in the SEM pictures (Fig. 4.3). The slight difference between each surface treatment is within the experimental error of the DMA test. The reason that the effect of the surface treatment is not obvious is because that the amplitude of the DMA test is 15 $\mu m$, which is so small that everywhere in the composite is in the linear range of small-deformation. This small deformation is not enough to cause extra shearing or debonding at the interface, and the difference of the overall viscoelastic properties will not be apparent until there
is local large deformation or displacement at the interface. For small-deformation tests, most of the deformation in the composites is carried by the polyurea matrix due to the significant difference of the moduli for the matrix and filler material, which explains the similar viscoelasticity for the four types of PUMG samples.

From this DMA result, we know that for small deformation applications such as acoustic wave propagation, the interface bonding strength does not significantly affect the viscoelastic properties of the PUMG composite. Thus for small-deformation applications, as-received milled glass can be used to fabricate PUMG composite and surface treatment will not cause much difference in its viscoelastic moduli.

Future research that includes larger deformation could be conducted for these silane-treated PUMG composites and the effect of the surface treatment could be observed.

Figure 4.4: DMA storage and loss Young’s moduli of PUMG composites for the four types of treatments. “AP” represents the control group washed by piranha solution.
4.1.5 Polyurea-glass interface pull-up test

In order to quantitatively estimate the tensile strength of these interfaces, a polyurea pull-up test was designed. The pull-up test sample had two pieces of aligned polyurea cast on both sides of the surface-treated glass plate. A metal slip was cast in each piece of polyurea for clamping the sample during the tension test. The nominal area of the polyurea-glass interface (one side) was 1.13 cm$^2$. The cast polyurea pull-up test samples were cured in the environmental chamber where humidity was controlled at 10% for at least 2 weeks before testing. The pull-up tests were conducted on Bose Electroforce 3200 mechanical tester, shown in Fig. 4.5. The tensile load ramped up from 0 N in a rate of 0.5 N/s until failure at the interface or yielding in the polyurea occurred.

For all the surface treatments except for the amine surface treatment, failure occurred at the interface. For the covalent-bonded interface, the pull-up test stopped due to the yielding of polyurea, while no debonding at the interface was observed.

Using the experimental data, the strength of the interface can be estimated as:
\[ \sigma_f = \frac{F_f}{A} \] (4.1)

assuming the stress distribution across the interface is uniform, where \( F_f \) is the failure load, and \( A \) is the area of the interface.

The result of the pull-up test is shown in Fig. 4.6. In consistent with SEM observation (Fig. 4.3), the control group and the urea surface treatments have similar tensile strengths because they both form hydrogen bonds between the glass and polyurea. The interface strength of aliphatic surface treatment is the lowest, because Van de Waals force is significantly lower than that of hydrogen bond. The amine surface treatment undoubtedly created the strongest interface by forming covalent bonds, even though the test did not proceed until failure at the interface was observed since polyurea started to yield first.

The pull-up test is a semi-quantitative estimation for the tensile strength of the interface. But it shows the drastic difference of the tensile strengths for various surface treatments.

4.1.6 Single-fiber fragmentation test

The shear properties of polyurea-glass interface were tested by single-fiber fragmentation, which was a commonly-used method to estimate the shear strength of the interface between the fiber and the polymer, most commonly for rigid polymers [20]. However, utilizing the transparency of polyurea, single-fiber fragmentation test is also applicable for the polyurea-glass system.

In this part of the study, single-fiber fragmentation samples were fabricated by casting a surface-treated single glass fiber along the axial direction of the dog-bone-
Figure 4.6: Polyurea-glass pull-up test: the average tensile strength of each type of polyurea-glass interface with its bonding strength modified.

The shear strengths of the polyurea-glass interfaces were calculated by analyzing the data of single-fiber fragmentation.

The photoelastic setup of the single-fiber fragmentation test is shown in Fig. 4.7. As can be seen from the pictures, when the polarizing filters were not placed, the fiber in the sample was invisible, and the fiber fragmentation process could not be observed. However, when a set of polarizing filters was placed on the back and the front of the sample with 90° difference in their polarizing directions, the stress concentration in the sample became clearly visible by the photoelastic effect, and the fiber fragmentation process could be observed.

Fig. 4.8 shows the various stages of the fiber fragmentation for the three types
The glass fiber used in this study was Owens Corning Type 30 E-glass fiber. It was cast at the center of a 8 cm long dog-bone-shaped polyurea tension test sample in a silicone mold. The mold was covered by a surface-treated non-stick glass plate (see Appendix C for the non-stick glass plate surface treatment) to ensure the flatness of the sample. The single-fiber fragmentation samples were fully cured for two weeks in the environment chamber, in which relative humidity was controlled at 10%. Single fiber fragmentation tests were conducted on the BOSE ElectroForce 3200 Test Instrument. The displacement rate of the tension test was 0.1mm/s after 5 seconds of dwelling time, until the fragmentation reached its saturation state. The saturation state was the state when there was no further fiber fragmentation when the stress/strain in the polyurea matrix continued to increase. Real-time photoelastic videos were recorded and the strains were measured by digital image correlation.

Considering the equilibrium condition of a fiber segment at its critical length, assuming uniform shear stress at the interface between polyurea and fiber, the shear
Figure 4.8: The process of fiber fragmentation with respect to time for the three types of the polyurea-glass interfaces.

strength at the interface can be approximated as:

$$\tau = \frac{\sigma_f \cdot d}{2l_c}$$  \hspace{1cm} (4.2)

where $\tau$ is the shear strength, $\sigma_f$ is the fiber strength, $d$ is the fiber diameter, and $l_c$ is the critical fiber length. Fiber strength $\sigma_f$ is a function of fiber length. The fiber model used in this study to calculate $\sigma_f$ is from Risø National Laboratory [20]. It is a fiber model for standard glass fiber with diameter of 16 $\mu$m. Critical fiber length $l_c$ is approximated as $\frac{4l}{3}$, where $l$ is the average fiber length when fiber fragmentation reached its saturation state.

The fiber model by Risø National Laboratory is written as [20]:
Figure 4.9: Critical fiber lengths and the average shear strengths measured by single fiber fragmentation test for the three types of surface treatments that graft aliphatic chains, urea groups and amine groups on the glass surfaces to bond with polyurea through Van de Waals force, hydrogen bonds and covalent bonds respectively.

\[
\sigma_f(L) = \sigma_0 \left( \frac{L_0}{L} \right)^{1/m}
\]

where \( \sigma_0 = 1680 \text{MPa} \), \( L_0 = 20 \text{mm} \), and \( m = 4.4 \).

This fiber model shows that the fiber strength is a function of fiber length. The longer the fiber length the weaker the fiber strength. It is due to the distribution of fiber defects along its length, and a long fiber is more likely to have a weaker point.

From the saturation fiber length, the critical fiber length and average interfacial shear strength are calculated, shown in Fig. 4.9. The trend of the average shear strength is the same as the result of the polyurea-glass pull-up test which approximates the tensile strength of the interfaces (Fig. 4.6). Similar to the pull-up test, this shear strength can only be regarded as the average shear strength, but not the point-wise local shear strength at the interface.

One of the important plots that single-fiber fragmentation test gives is the crack density plot. It is the crack density observed during the test as a function of tensile strain in the polyurea matrix.
The true tensile strain in the polyurea matrix is calculated by

\[ \varepsilon_T = \int \frac{dl}{l} = ln \frac{l}{l_0} = ln \left( \frac{l_0 + \Delta l}{l_0} \right) = ln(1 + \varepsilon_E) \]

where \( \varepsilon_T \) represents true strain and \( \varepsilon_E \) represents engineering strain. \( l_0 \) is the original length, and \( \Delta l \) is the length change.

And the average tensile stress at the cross-section of the single-fiber fragmentation sample can be calculated as:

\[ \sigma_T = \frac{F}{A} = \frac{F e^{\varepsilon_T}}{A_0} \]

For the three types of surface treatments, the crack density plot is shown in Fig. 4.10. This plot provides information of the whole fiber fragmentation process, and can be used for further analysis for the interface properties.

### 4.1.7 Modeling of the polyurea-glass interface

More information about the polyurea-glass interface can be extracted from the single-fiber fragmentation test, not limited to the estimated shear strength. When calculating the estimated shear strength using Eq. 4.2, the distribution of the shear stress along the fiber is not considered. However, in reality, the shear stress is higher at the ends of the fiber segments than at the half-span of the fiber segments, and the shear stress near the ends of the fiber segments reaches the yield stress or failure stress earlier than the positions near the half-span of the fiber segments. Thus in the single-fiber fragmentation test, failure or matrix yielding is observed propagating from the ends of the fiber segments towards the half-span of the fiber segments.
Figure 4.10: Crack density as a function of tensile strain in the polyurea matrix for the three types of surface treatment.

For the weaker interfaces with aliphatic or urea surface treatments, separation at the interface is observed along the glass fiber-polyurea interface; for the strong interface with amine surface treatment, yielding in the polyurea matrix is observed, as shown in Fig. 4.11. The illuminated zones change along the fiber length in the photoelastic pictures as the single-fiber fragmentation test proceeds. A sudden dimming in the illuminated area means there is debonding at the interface. This debonding occurs in the samples with aliphatic or urea surface treatments, and the propagation of the debonding along the fiber length is much faster for aliphatic surface treatment comparing to the sample with urea surface treatment. For amine surface treatment, the illuminated zones gradually fade out towards the center of the fiber segments due to the yielding and relaxation in the cohesive zone in the vicinity of the polyurea-fiber interface.

Since there is a gradient of stress and strain along the fiber fragments, by
Figure 4.11: Two interface failure modes in the single-fiber fragmentation test. Interface debonding is observed for the aliphatic and urea surface treatments, and yielding in the polyurea is observed for the amine surface treatment.
measuring the strain in the polyurea matrix, the speed of the interface debonding or the interface yielding, interface models can be developed for the three types of interfaces. Modeling of the covalent-bonded polyurea-glass interface will be discussed in the following of this subsection. The two types of weaker interfaces can be studied in future research by including the debonding effect.

For each fiber fragment, assuming the force-displacement relation at the interface obeys the shear-lag model:

\[
\frac{dp}{dx} = H(u - v) \tag{4.4}
\]

where \( p \) is the axial load of the fiber, \( x \) is the position along the fiber length, \( u \) is the displacement in matrix at position \( x \), \( v \) is the displacement in the fiber at position \( x \) and \( H \) is a constant representing the stiffness of the interface. The unit of \( H \) is \( Pa \).

Inside the fiber, assuming the distribution of the tensile stress is uniform for a cross-section, \( p \) can be represented as:

\[
p = EA \frac{dv}{dx} \tag{4.5}
\]

where \( A \) is the cross-section area of the fiber.

The strain in the matrix (\( \epsilon \)) is equal to the displacement gradient:

\[
\frac{du}{dx} = \epsilon \tag{4.6}
\]

From Eq. 4.4-4.6, get the second derivative of \( p \):
\[
\frac{d^2 p}{dx^2} = H \left( \frac{du}{dx} - \frac{dv}{dx} \right) = H \left( \epsilon - \frac{p}{EA} \right)
\]  
(4.7)

where \( E = 75 \text{GPa} \) and \( A = 1.2566 \times 10^{-11} \text{m}^2 \) for standard E-glass fiber with diameter of 16\( \mu \text{m} \).

Load distribution in the fiber can be obtained by solving this Eq. 4.7 with the boundary conditions:

\[ p = 0 \text{ at } x = 0 \text{ and } x = l \]

Knowing the stress distribution along the fiber length, in order to simulate fiber fragmentation process, a fiber strength model is needed for finding the location of the next breaking point. The fiber model used in the simulation is for standard E-glass fiber, developed by Risø National Laboratory in Denmark [20]:

\[
\sigma_f(L) = \sigma_0 \left( \frac{L_0}{L} \right)^{1/m}
\]  
(4.8)
where $\sigma_0 = 1680\text{MPa}$, which is the characteristic strength. $L_0 = 20\text{mm}$, which is the gauge length of the fiber model. $m = 4.4$.

For example, when the fiber length is 0.04 m and the strain in the polyurea matrix is 0.019, the stress distribution along the fiber is shown as the blue curve in the left plot of Fig. 4.12. The maximum stress is always at the half-span of the fiber, but the new break does not necessarily happen at the half-span of the fiber, since the defects or the weakest point of the fiber are randomly distributed.

In the simulation, the critical stress $\sigma_c$ is defined as:

$$\sigma_c = (1 - \delta)\sigma_f$$

(4.9)

As the strain increases, the maximum stress of the fiber segment increases until it reaches the failure stress, $\sigma_f$, calculated by Eq. 4.8. $\delta$ is set to be 0.001, and the critical zone is where $p(x) \geq \sigma_c$.

In critical zone where new break can happen, due to the random distribution of the defects in the fiber, the location of the new fiber breakage is assumed to be randomly positioned in the critical zone:

$$\text{new breakage location} = \text{random} \left( x \mid p(x) \geq \sigma_c \right)$$

(4.10)

Assuming there is a maximum shear stress at the interface and above that polyurea starts to yield, we have:

$$\frac{dp}{dx} = H(v - u) \leq M$$

(4.11)

If knowing $H$ and $M$, the whole process of the single fiber fragmentation can
be simulated, and the flow chart of the programming for the simulation is shown in
Fig. 4.13.

From the simulation result of single-fiber fragmentation, a plot of crack density
with respect to the tensile strain in the polyurea is obtained. Comparing it with the
experimental result, a best fit of $M$ and $H$ can be obtained.

$H$ is related with the shear modulus of the polyurea, $\mu$, and the thickness of
the cohesive layer, $a$, as shown in Fig. 4.15; $M$ is related with the maximum shear
strength of the interface $\tau_{\text{max}}$. The cohesive law of the interface can be fully expressed
if $a$ and $\tau_{\text{max}}$ are known since the shear modulus of polyurea can be estimated from the
load-frame data assuming that $E \simeq 3G$ at room temperature and the strengthening

**Figure 4.13:** Flow chart of the simulation for single-fiber fragmentation.
The shear cohesive law of the covalent-bonded interface which relates the shear stress $\tau$ with the relative displacement $u - v$ is shown in Fig. 4.14. In the cohesive law, the maximum shear stress of the interface $\tau_{max}$ is equal to:

$$\tau_{max} = \frac{M}{2\pi r}$$  \hspace{1cm} (4.12)

And the slope of the cohesive law before reaching the maximum shear stress can be expressed as:

$$h = \frac{H}{2\pi r} = \frac{2\mu}{a}$$  \hspace{1cm} (4.13)

A comparison of the crack density plot between the simulation and experiment is shown in Fig. 4.16, where $\tau_{max}$ is 5.8 MPa and the thickness of the cohesive layer is 46 $\mu m$.

Thus, by simulating the single-fiber fragmentation of the covalent-bonded interface and comparing with the experimental data, the shear cohesive law of the interface can be obtained.
Figure 4.15: Cohesive zone thickness $a$. The blue area represents a part of the glass fiber, and the yellow area is a part of the polyurea. $x$ is the axial direction of the fiber.

Figure 4.16: Comparison between experimental and simulation results of the crack density as a function of the strain in the polyurea matrix.
• The derivation of Eq. 4.13:

Assuming the shear stress distribution within the cohesive layer \( a \) (Fig. 4.15) is linear to the distance away from the polyurea-glass interface, the displacement field \( u_x \) in the cohesive zone of polyurea is parabolic.

In the cohesive layer, let:

\[
  u_x = c_1 z^2 + c_2 z + c_3
\]

The boundary conditions are:

\[\begin{align*}
  u_x &= u_{fiber} \text{ at } z = 0, \\
  u_x &= u_{matrix} \text{ at } z = a, \text{ and } \\
  \frac{du_x}{dz} &= 0 \text{ at } z = a.
\end{align*}\]

Solve Eq. 4.14 and get:

\[
  c_1 = \frac{u_{fiber} - u_{matrix}}{a^2}
\]

\[
  c_2 = -2 \frac{u_{fiber} - u_{matrix}}{a}
\]

\[
  c_3 = u_{fiber}
\]

Thus Eq. 4.14 can be written as:

\[
  u_x = \frac{u_{fiber} - u_{matrix}}{a^2} z^2 - 2 \frac{u_{fiber} - u_{matrix}}{a} z + u_{fiber}
\]

Stress and strain at the interface where \( z = 0 \):

\[
  \epsilon_{xz} = \frac{1}{2} \left. \frac{du_x}{dz} \right|_{z=0} = -\frac{u_{fiber} - u_{matrix}}{a}
\]
\[
\sigma_{xz} = 2\mu \varepsilon_{xz} \bigg|_{z=0} = -2\mu \frac{u_{\text{fiber}} - u_{\text{matrix}}}{a}
\]  

(4.20)

Consider the equilibrium of the fiber, get:

\[
\frac{dp}{dx} = -2\pi r \sigma_{xz} = 4\pi r \mu \frac{u_{\text{fiber}} - u_{\text{matrix}}}{a} = H(u_{\text{fiber}} - u_{\text{matrix}})
\]

\[
\frac{4\pi r \mu}{a} = H = 2h\pi r
\]  

(4.21)

\[
h = \frac{2\mu}{a}
\]  

(4.22)

In reality, polyurea is a viscoelastic material, and \(M\) and \(H\) are related with the strain rate. The current study does not include the strain rate dependence and this part could be studied in the future work.

### 4.2 Polyurea-metal interface

Polyurea is widely applied as a coating material on the metal surfaces. Without surface treatment, the metal and polyurea cannot form a strong bond. Experiments have shown that if polyurea is coated on the back side of a metal plate, it can effectively protect the metal plates from impact loading [3]. But delamination has been observed on the impacted samples. Even for small-deformation acoustic applications, polyurea-metal interface needs to be strengthened. For instance, polyurea-metal layered composite can delaminate at the interface after a moderate temperature change, due to the stress caused by the difference in the thermal expansion coefficients between
metals and polymers. In this section, the modification of polyurea-metal interface is experimented in terms of how to strengthen the interface between polyurea and metal.

For metals that form a passive oxide layer, silanol groups in the hydrolyzed organosilanes can attach to the hydroxyl groups on the metal oxide and form covalent bonds; for metals that do not form a passive layer, chelation chemistry is usually used to bond with the metal atoms [23]. Diagrams of the two types of bonding mechanism are shown in Fig. 4.17.

### 4.2.1 Surface treatment of aluminum

Aluminum forms a densely packed oxide layer on the surface, which makes aluminum very stable even in an aqueous environment. The aluminum oxide makes the aluminum surface similar to the glass or silica surface in terms of the functional groups that can be react with organosilanes.

Most of the silanes that can be used for the glass surface treatment can also be applied for the aluminum as well. The three types of silanes mentioned in the
first section of this chapter can be used for aluminum surface treatment under similar procedure and create the similar adhesion to the polyurea. The procedure of surface cleaning using piranha solution cannot be applied for cleaning most metal surfaces.

In order to increase the bonding strength between polyurea and aluminum, (3-aminopropyl)trimethoxysilane can be used to treat the aluminum surface. If for decreasing the bonding strength, trimethoxy(octyl)silane can be used for the aluminum surface treatment.

4.2.2 Surface treatment of stainless steel

The difference between carbon steel and stainless steel is whether there is a passive layer on the surface of the alloy. The carbon steel does not form a densely packed oxide layer on the metal surface thus oxygen and water can easily penetrate and attack the metal atoms underneath. However, due to the high content of the chromium in the stainless steel, there is an effective passive layer on the stainless steel surface which makes stainless steel more corrosion-resistant.

For stainless steel, even though large percentage of surface area is covered by passive layer, we still assume that both metal oxides and uncovered metal atoms exist on the stainless steel surface since the corrosion resistance varies for various types of stainless steel. Thus, for creating a strong bonding between polyurea and stainless steel, n-[3-(trimethoxysilyl)propyl]ethylenediamine (AEAPTMS) surface treatment is used. Its molecular structure is shown in Fig. 4.18. Both ends of this organosilane can react with the stainless steel surface, one through chelation with metal atoms and the other by reacting with the hydroxyl groups. The silanol groups can also connect and form a network of the organosilane, and the amino groups can react with the
Figure 4.18: The structure of AEAPTMS, the surface treatment reagent for stainless steel surface.

isocyanate to covalently bond with polyurea. Fig. 4.19 shows a simplified diagram of the organosilane network of AEAPTMS that bonds the steel with the polyurea.

In practice, the AEAPTMS surface treatment was successfully applied in the fabrication of the layered composite material for underwater sonar stealth. AEAPTMS was applied on the steel plates before assembling a layered composite material made of layers of stainless steel, PU\textsubscript{20\%MG} and PU\textsubscript{40\%PMB} (Fig. 4.20). The effectiveness of this surface treatment was obvious. When epoxy was used to bond the stainless steel layers with the composite layers, delamination at the interface occurred when the assembled layered sample was cooled from room temperature down to 10 °C. However, after using AEAPTMS surface treatment on stainless steel and reassembling the layers using polyurea as the glue, the layered composite material stayed intact after thermal cycling from room temperature to −15°C.

4.2.3 Surface treatment procedure for metal

For organosilanes that have the alkoxy functionality, water is needed for the hydrolysis process. The surface treatment procedure for aluminum and stainless steel is as follows:

1. Thoroughly clean the metal surface by soap and water and acetone
Figure 4.19: A simplified diagram showing the mechanism of AEAPTMS surface treatment for bonding polyurea with stainless steel.

Figure 4.20: Layered composite material designed for underwater sonar stealth. The diameter of the sample is 8 inch.
2. Dry the metal in the oven at 110°C

3. Prepare the solvent for silane: 95% ethanol+5% water

4. Add the appropriate amount of silane with stirring to prepare a silane solution of 0.1mol/L concentration

5. Keep stirring for 5 minutes to allow hydrolysis and silanol formation

6. Soak the metal in the silane solution for 2 minutes

7. Rinse the metal gently with ethanol twice

8. Cure the treated metal surface in oven for 1 hour at 110 °C

The treated surface is stable and can be stored in a clean environment. The surface-treated metal surface should be protected from contamination, since contamination can cover the functional groups on the surface and affect the effectiveness of the surface treatment.

### 4.3 Summary

In this chapter, the modification, characterization and modeling of polyurea-glass interface were studied; and the surface treatments for modifying polyurea-metal interface were discussed.

Three types of glass surface treatments were applied for creating weak, intermediate and strong bonding between polyurea and glass through Van de Waals’ force, hydrogen bond and covalent bond, respectively. The interface modifications were examined under SEM, and the normal and shear strength of the interface were characterized by the pull-up test and single-fiber fragmentation test respectively. All test results showed that the surface treatments were successful. As a new method to utilize the single-fiber fragmentation data, an interface shear cohesive law was devel-
oped for the covalent-bonded polyurea-glass interface, by comparing the simulation and the experimental results of the single-fiber fragmentation.

Due to the fact that metal is a common substrate for polyurea, the surface treatment of metal is also discussed considering different types of metal surfaces.

The knowledge obtained from this chapter can be utilized in the fabrication of polyurea composite materials to control the interface adhesion.

This chapter, in part, appears in the conference proceeding Tailored Polyurea-Glass Interfaces and the Characterization by the Single-Fiber Fragmentation, in *ASME 2013 International Mechanical Engineering Congress and Exposition. American Society of Mechanical Engineers*, 2013, by Z. Jia, R. Rawal, J. Isaacs, and S. Nemat-Nasser. I would like to thank Office of Naval Research for sponsoring this part of research, and I also would like to thank all my coauthors for their collaborations and contributions.
Chapter 5

Novel characterization technique for polyurea and its composites at mid-level (kHz) frequencies: acoustic ball impact (ABI) test

Two common measurement techniques for the viscoelastic properties of elastomeric polymers are dynamic mechanical analysis (DMA) and ultrasonic wave measurement, for low and high frequencies respectively. However, the existing characterization techniques cannot cover the entire frequency range of polyurea’s relaxation, which spans more than 10 decades in the logarithmic scale. An estimation method based on DMA data has been discussed in Chapter 3 for modeling the polyurea and its composites. However, estimation involves assumptions, and direct measurement is preferred if precise viscoelastic properties are required. The mid-level frequencies (kHz) is a challenging frequency range for characterizing the viscoelastic properties of
polyurea, due to the fact that large sample size is required and the dissipative nature of polyurea.

In this part of study, we modify a split Hopkinson pressure bar using ball impact to measure viscoelastic properties of polyurea at mid-level (kHz) frequencies, which fills the frequency gap between dynamic mechanical analysis and ultrasonic wave measurement. A temperature chamber is incorporated into the test setup, considering the viscoelastic properties of polymers are usually temperature-sensitive. The measured storage and loss Young’s moduli are compared with the master curves developed using experimental data of dynamic mechanical analysis. This novel testing technique is not limited to characterization of polyurea, it can also be applied for other similar materials.

5.1 Introduction of ABI test

Elastomeric polyurea has both excellent thermal and mechanical properties. It has a wide frequency range of relaxation, which spans more than 10 decades in the logarithmic scale [35]. It is tough and dissipative and is excellent for managing shock/impact-induced energy [7]. Its viscoelastic properties are highly sensitive to frequencies. Existing characterization techniques are not sufficient to directly measure its viscoelastic properties for the entire frequency range of its relaxation.

At the low frequency end, viscoelastic properties can be measured by dynamic mechanical analysis (DMA). The operating frequency range of modern DMA is in the order of $10^{-2}$ to $10^2$ Hz according to TA Instruments. For the high frequency end, ultrasonic wave measurement is the main characterization technique. Normally testing frequency range of ultrasound spans within 50 kHz to 200 MHz [74]. The theories
of ultrasonic wave measurement can be found in [73, 41, 66]. Measurement at low
frequency from 1 to several kHz is very challenging for ultrasonic wave measurement
since it requires large piezoelectric material and it also requires large transmitting
media between the transducer and the sample.

In order to fill the frequency gap between DMA and ultrasonic wave mea-
surement for polyurea, we have developed a modified split Hopkinson pressure bar
(SHPB) using ball impact to measure viscoelastic properties of polyurea at mid-level
(kHz) frequencies. This measurement technique is later on referred to as acoustic
ball impact (ABI) test. Unlike standard operation of SPHB, we use an aluminum
striker ball instead of a striker bar to generate the incident pulse. The impact force
profile can be accurately estimated from Hertzian contact solution, which is used as
a theoretical guidance to adjust the testing frequency content of the input signal. We
also integrated a temperature chamber, which enables us to test from -50 °C to 50
°C, considering viscoelastic properties of polymers are usually temperature-sensitive.
Two tests with different sample thicknesses are required for ABI test. The sample in
each test is cylindrical and has the same diameter as the aluminum bars. Signals are
measured using two ultra-sensitive semiconductor strain gages placed at the half-span
of the two aluminum bars.

Incident and transmitted signals are analyzed using phase spectral analysis
(PS) [62, 38, 53, 37] and transfer matrix method [47] to find wave speed and attenu-
ation in the material. Young’s storage and loss moduli are calculated and compared
with the frequency domain master curves developed from the data of dynamic me-
chanical analysis (DMA). Also, the trend of the attenuation measured by ABI test is
compared with the attenuation calculated from DMA data.
Table 5.1: Material properties of the aluminum bars, sample and steel confinement tube for the finite element simulation.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Aluminum Bars</th>
<th>Polyurea (elastic)</th>
<th>Steel Tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($\rho$) [kg/mm$^3$]</td>
<td>$2.82 \times 10^{-6}$</td>
<td>$1.09 \times 10^{-6}$</td>
<td>$7.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>Young’s Modulus ($E$) [GPa]</td>
<td>73.364</td>
<td>0.3</td>
<td>200</td>
</tr>
<tr>
<td>Poisson’s Ratio ($\nu$)</td>
<td>0.334</td>
<td>0.45</td>
<td>0.3</td>
</tr>
</tbody>
</table>

This novel ABI test is not limited to polyurea characterization, it can also be applied for other similar viscoelastic materials.

5.2 Finite element simulation

Finite element simulations of the wave propagation are conducted on LS-DYNA. The test setup of two 4-feet-long aluminum bars with one 10 cm polyurea sample sandwiched in between is simulated, as shown in Fig. 5.1. A 2D axi-symmetric model is used to simulate the whole test setup. The simulation is computed explicitly. All materials are assumed elastic.

The material properties used in the simulation are listed in Tab. 5.1, and the units for the simulation is listed in Tab. 5.2. The mesh size is 1 mm and the total energy during the entire wave propagation process is conserved.

The aluminum striker ball is not included in the simulation. Instead, initial velocity is prescribed on each node of the left end of the first aluminum bar. The initial velocity pulse shape is shown in Fig. 5.2. It is a stabilized soliton propagating in a granular chain. The reason to choose this bell-shaped input signal is because this
type of signal has smooth transition at both ends of the pulse, which minimizes high
frequency noise and is essential for obtaining clear and smooth measurement signals.
Input signals such as several cycles of sine wave cannot be used for this test, since
the sudden change at the ends of the signal complicates the measurements.

In the finite element model shown in Fig. 5.1, or Fig. 5.3, the length of
each aluminum bar is 4 feet, the length of the sample is 10 cm. Explicit analysis is
conducted. It should to be noted that in Fig. 5.3, the displacement is magnified for
100 times for clearly showing the deformation in each part of of the model.

Two types of radial boundary conditions of the sample are simulated. The first
case is radially confined from expansion, and the second case is radially unconfined, as
shown in Fig. 5.3. In this figure, the finite element parts before and after deformation
are shown for the unconfined and confined case. The deformed parts represent the
moment when the first compression pulse passes through the sample. The blue area
is under compression and the red area is under tension. The radial confinement is
prescribed by a steel tube, the inner diameter of which is the same as the diameter of
the sample. All nodes at the interface between the sample and the aluminum bars are
tied, and automatic_surface_to_surface_2D contact card is used between the sample
and the steel radial confinement. For the unconfined and confined test, the axial
stresses in y direction calculated at the half-span of the aluminum bars are shown in
Fig. 5.5 and 5.6. Bar 1 is the incident bar and Bar 2 is the transmission bar. For the
radially confined case, zero friction is assumed between the steel confinement and the
sample.

In the actual experiment, the radially confined test is not conducted since
the friction-free radial condiment is difficult to apply. In the simulation, the radially
confined case helps to understand what each peak in the signals physically means. The blue curve is the axial stress at the mid-span of the incident bar, and the red curve is the axial stress at the mid-span of the transmission bar. To help explain the signal, a schematic drawing of the aluminum bar and polyurea is shown in Fig. 5.7, where each interface is numbered. The first peak in the blue curve in Fig. 5.5 and 5.6 is the incident signal. Due to the much lower impedance of polyurea comparing to the aluminum bar, the first reflected pulse, which is the second peak of the blue curve, reflected at interface 2 becomes tension. The first transmitted pulse is the first peak in the red curve. The first transmitted pulse is easier to identify for the radially confined case, while for the unconfined case, the first transmitted signal has lower amplitude and a tail which is due to the radial displacement and reflection in the polyurea.

This tail due to the radial displacement could be seen in Fig. 5.3, where small zones of tension and compression follows the main pulse in the sample for the unconfined test. This pulse tail was also observed in Fig. 5.4, when the two interfaces between polyurea and aluminum are not tied, which shows the pulse tail is not due to the tied interface between the sample and the aluminum bars. Energy dissipation is not considered in the simulation, but in the real experiment, when polyurea and its composites are highly dissipative, this tail in the transmission pulse in the unconfined test is reduced to a slow decrease of the compression pulse or a much smaller tail in the real experiment, as shown in Fig. 5.12, which will be discussed more in the following of this chapter.

Since the speed of the pressure wave in a solid is coupled with the Poisson’s ratio, the diameter of the sample bar will affect the measured wave speed. By com-
Figure 5.1: 2-D axi-symmetric simulation for the ABI test. The FE model includes three parts, which are the two aluminum bars and one 10 cm sample between the two aluminum bars.

Figure 5.2: Input signal for the FE simulation: initial velocity of each node on the left end of the incident aluminum bar.

Comparing the nominal wave speed, $\sqrt{E/\rho}$ or $\sqrt{L/\rho}$, where $E$ is the Young’s modulus and $L$ is the longitudinal modulus, with the wave speed measured from the simulation signals calculated at the half-span of the aluminum bars for the unconfined and confined test, using the peak of the first reflected signal measured in Bar 1 and the first peak in Bar 2. With less than 5% of error, the peak-to-peak wave speed in the 10 cm unconfined polyurea is equal to wave speed $\sqrt{E/\rho}$, where $E$ is the Young’s modulus, and the peak to peak wave speed in the radially confined polyurea is equal to $\sqrt{L/\rho}$, where $L$ is the longitudinal modulus. This estimation shows that for an unconfined test, the compression wave is propagating with bar speed, $\sqrt{E/\rho}$, in a 10 cm or longer polyurea sample.
Figure 5.3: Test pulse traveling through sample for unconfined and confined test.

Figure 5.4: Test pulse traveling through sample when the interfaces are not tied.
Figure 5.5: Unconfined test: axial stress at the mid-span of the two aluminum bars.

Figure 5.6: Confined test: axial stress at the mid-span of the two aluminum bars.
5.3 Experimental setup

The split Hopkinson pressure bar (SHPB) measurement is a widely used experiment technique to study the behavior of metallic material at high strain rates [31, 39, 28, 19]. However, if the specimen is a soft material, which has a much lower impedance comparing to steel, the transmitted signal will contain a high level of noise if tested using a conventional steel SHPB [15]. There are also polymer SHPB developed for solving the issue of impedance mismatch and these polymers bars can provide measurable transmitted signal [80, 79, 64]; however it requires extensive effort and mathematical treatment of the signals obtained from the experiment due to the geometrical and material dispersion in the viscoelastic bars [80, 6].

To avoid material dispersion in the bar, two aluminum bars (7075-T6) of length 1.22 m and diameter 0.019 m (3/4 inch) are used as the wave propagation media in the ABI measurement. Comparing to steel bars, aluminum bars give larger signals for the same level of stress because the impedance difference is less for polyurea and aluminum [15].

The incident pulse is generated by the impact between an aluminum ball and the incident bar. The striker ball is made by the same grade of the aluminum as the aluminum bars (7075). The impact between the aluminum ball and aluminum bar generates an incident pulse which is a clear bell-shaped signal, and the amplitude and
frequency content of the signal could be controlled. The force-displacement relation for the impact between ball and plane is discussed in [69, 48], and the motion of equation can be found in [55, 29].

To control the ball velocity at impact, we use a simple ball release system with a three-prong clamp to hold and release the ball, as in Fig. 5.8 (a). The ball is suspended by two strings in the form of V-shaped pendulum. The lengths of the strings and the height of the suspension pivot bar are adjustable to provide the desired ball impact speed and force (see figure 5.8). In order to increase measurement sensitivity, two encapsulated Kulite G S/AGP-1000-300 semiconductor strain gages, which can operate up to 5000 microstrain in tension 7000 microstrain in compression [33], are bonded on the surface at the half-span of each bar (location S1 and S2) in the form of half Wheatstone bridge circuit (see Fig. 5.8 (b)). The measured strain signals at S1 and S2 are sent to the digital oscilloscope (Tektronix DPO 3014). To perform the ABI measurement at various temperatures, the temperature chamber, Sun Electronic System model ET1, is integrated into the measurement system (see figure 5.8 (a)).

5.4 Sample fabrication for ABI test

5.4.1 Fabrication of pure polyurea samples

Polyurea samples are fabricated using Isonate 143L (Dow Chemical Company) and Versalink P-1000 (Air Product and Chemicals, Inc.). The stoichiometric ratio of Isonate 143L and Versalink P-1000 is controlled at 1.05 in the fabrication [10]. The 5% extra isocyanate ensures the completion of polymerization.
Figure 5.8: (a) Real experimental setup (b) Schematic diagram of experimental setup
The two components (Isonate 143L and Versalink P-1000) are first degassed at 1 torr and at the same time stirred by magnetic stir bars for one hour until most of the air bubbles are removed. After the degassing process, the appropriate amount of Isonate 143L is quickly added into Versalink P-1000, and the mixture is degassed for an additional 5 minutes under the vacuum. The mixture is then transferred into the 1 foot long Teflon pipe using the experimental setup shown in the schematic drawing of Fig. 5.9 (a). The inner diameter of the Teflon pipe is 0.75 inch, same as the aluminum bar of the test setup. The valve at the bottom of the Teflon pipe is turned off at the end of the suction when the Teflon pipe is full. The Teflon pipe is set in the upright position to let air bubbles float to the top. The sample is cured in the desiccant chamber for two weeks before cutting and demolding.

The 1 foot long Teflon pipe with polyurea sample cast and cured inside is then machine-cut into various lengths (Fig. 5.9 (b)). Both ends of the polyurea samples are sanded with high accuracy such that the two ends of each sample are smooth and perpendicular to the axial direction. The final sample lengths are 4 cm, 6 cm, 8 cm, and 10 cm. These samples can be stacked up to make additional lengths for the test.

From the same batch of pure polyurea, three DMA samples of nominal size $3\,mm \times 10\,mm \times 30\,mm$ are made and tested on TA2980 dynamic mechanical tester. The averaged DMA data are used for developing master curves to compare with the ABI measurement [35].

### 5.4.2 Fabrication of polyurea composites samples

Long bar samples of polyurea composites are fabricated using a different casting method. Two types of polyurea composite samples are made. They are polyurea
with 20% volume fraction of milled glass (PU$_{20\%}$MG) and polyurea with 40% volume fraction of phenolic microbubbles (PU$_{40\%}$PMB). The details of the degassing and mixing procedure of this two types polyurea composites have been discussed in Chapter 2.

Since the density of milled glass is higher than the density of pure polyurea, and the density of phenolic microbubbles is lower than pure polyurea, the method in Fig. 5.9 (a) would cause density gradient along the composite bar. Thus a new type of mold is designed for casting PU$_{20\%}$MG and PU$_{40\%}$PMB, as shown in Fig. 5.10.

The left picture of Fig. 5.10 shows the assembly of the mold, and the right picture is a cast sample of PU$_{20\%}$MG. This mold contains two tubes, the outside transparent tube is 1.36 inch diameter polyethylene tube. The white tube is the Teflon tube, with inner diameter of 0.75 inch and outside diameter of 1 inch. Two glass buttons are borosilicate glass with diameter of 1.25 inch and thickness of 0.25 inch. These glass buttons are surface-treated by dichlorodimethylsilane purchased from Sigma-Aldrich to be non-stick with polyurea, and the smooth surface of the
glass ensures the flatness of the end surface of the bar sample, which is essential for the compression pulse transmission. The surface treatment for making the non-stick glass surface can be found in Appendix C. Two conical steel springs are placed between the red vinyl cap and the glass button to make sure that the glass button is in good contact with the Teflon pipe during the curing process. The wire thickness of the steel conical spring is 0.40 inch, and the length of which is 0.625 inch; the large diameter is 0.720 inch and the small diameter is 0.375 inch. Using the two tube system is because polyurea has a small volume reduction during the curing process, which will cause air bubbles if there is no material outside the inner tube to fill in the void formed by the volume reduction.

After the materials are degassed and mixed, the mixed slurry of PU\_20\%MG or PU\_40\%PMB is carefully filled inside the polyethylene tube, both outside and inside the Teflon tube. The glass buttons are carefully placed such that no air bubble is trapped inside the Teflon tube during the casting procedure. After placing the red vinyl caps, the entire mold is rotated in all directions for 30 minutes and cured overnight in the desiccant chamber before demolding. The rolling procedure is to prevent gradient properties due to the density difference between polyurea and filler materials. An assembled mold with PU\_20\%MG cast inside is shown in the right picture of Fig. 5.10.

From the same batch of PU\_20\%MG and PU\_40\%PMB, three DMA samples of nominal size $3mm \times 10mm \times 30mm$ are made for each type of composite, and tested on TA2980 dynamic mechanical tester.
Figure 5.10: Polyurea composites ABI sample fabrication. The left picture is a disassembled mold and the right picture is a assembled mold with PU_20%MG cast inside.

Figure 5.11: Bar samples of polyurea composite: polyurea with 20% milled glass (PU_20%MG), and polyurea with 40% phenolic microbubbles (PU_40%PMB).
5.5 Experimental measurements

Two tests with two different sample lengths are required for measuring wave speed and attenuation of the sample. In test 1, a short sample is placed inside the temperature chamber and inserted between the incident and transmission bars. The sample is aligned with the bars. Two thin cylindrical sleeves made of nylon tape are used for support and alignment between the sample and bars (see figure 5.8 (b)). Oil couplant is applied on all contact interfaces for better transmission of the pulse signal. The ball is set into place and held by the 3-prong clamp. The position of the pendulum system is adjusted such that the impact velocity of the ball is aligned with the axial direction of the aluminum bar and the impact location is at the center of the cross-section of the bar. This impact location is kept consistent for all tests. After reaching thermal equilibrium, the striker ball is released at the height of 0.33 m. The ball hits the incident bar at the left end. The wave propagates through the incident bar, the sample and the transmission bar. The incident and the reflected signals are measured by the strain gage S1 at the half-span of the incident bar and the transmitted wave is measured by the strain gage S2 at the half-span of the transmission bar. The signals are transmitted to a digital oscilloscope (Tektronix DPO3014) and recorded there (see figure 5.8 (b)). The same procedure is followed by test 2 using a longer sample. The transmitted wave signals recorded at strain gage S2 from the two tests with different sample lengths are used for data analysis.

For pure polyurea samples, ABI tests are performed from 223 K to 323 K with 10 K increments. For each testing temperature, the sample is equilibrated for 40 minutes before the ABI test. A complete testing table is shown in Tab. 5.3.

For polyurea composite samples (PUMG and PUPMB), ABI tests are only
Table 5.3: ABI test matrix for pure polyurea samples. Three sample pairs with varied length differences are chosen.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sample pairs</th>
<th>Tests per pair</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>223K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>233K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>243K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>253K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>263K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>273K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>283K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>293K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>303K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>313K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>323K</td>
<td>(10 cm, 14 cm), (10 cm, 16 cm), (10 cm, 18 cm)</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

c conducted at one temperature point at 10 °C.

5.6 Data analysis

5.6.1 Phase spectral analysis

At each testing temperature, the transmitted wave signals from the two tests with different sample lengths are converted to frequency domain using Fast Fourier Transform (FFT), and the complex amplitude is calculated, which contains the physical amplitude and phase of each frequency component in the transmitted signals. The wave speed and attenuation are calculated using the two equations [62, 38, 53]:

\[
c(f) = \frac{2\pi f (d_2 - d_1)}{\left(\phi_2(f) - \phi_1(f)\right)}, \quad (5.1)
\]

\[
\alpha(f) = -\frac{1}{(d_2 - d_1)}ln\left(\frac{A_2(f)}{A_1(f)}\right), \quad (5.2)
\]
where $c$ is wave speed; $f$ is frequency; the subscript 1 means test 1 (short sample) and the subscript 2 means test 2 (long sample). $d$ is the length of samples. $\phi$ is the unwrapped phase at frequency $f$. $\alpha$ is attenuation per unit length. $A$ is the absolute amplitude at frequency $f$ from tests 1 and 2, respectively. The Young’s storage and loss moduli can be obtained from [56]:

$$E' = \frac{\rho c^2 (1 - r^2)}{(1 + r^2)^2}, \quad (5.3)$$

$$E'' = \frac{2 \rho c^2 r}{(1 + r^2)^2}, \quad (5.4)$$

$$r = \frac{\alpha c}{\omega}, \quad (5.5)$$

$$E^* = E' + E'' i, \quad (5.6)$$

where $E'$, $E''$, and $E^*$ are Young’s storage, loss and complex moduli, respectively, $\rho$ is the density of the sample, $r$ is dimensionless parameter, and $\omega$ is angular frequency.

At each temperature, 6 tests are performed as listed in table 5.3. The averages are taken to calculate the wave speed, attenuation, Young’s storage, and loss moduli for a given frequency and temperature.

An example of the ABI test signals of pure polyurea is shown in Fig. 5.12, where (a) and (b) are the signals measured at S1 and S2; the two peaks in (c) are the incident and reflected signals cut from (a); (d) shows the transmitted signals which are cut from the signals in (b).
Figure 5.12: (a) Recorded signals at S1 on the incident bar, (b) recorded signals at S2 on transmission bar, (c) Incident and the first reflected signals at S1 on incident bar, (d) transmitted signals at S2 on the transmission bar.
5.6.2 Transfer matrix method

Transfer matrix calculation is an effective method to calculate wave propagation through a one dimensional layered composite based on the given geometries and properties of each layer in the composite [11, 47]. The displacement and stress at the left boundary of the sample can be related to the displacement and stress at the right boundary (see Fig. 5.7) by a matrix called transfer matrix.

\[ \begin{bmatrix} u_L \\ \sigma_L \end{bmatrix} = TM \begin{bmatrix} u_R \\ \sigma_R \end{bmatrix}, \]  

(5.7)

\[ TM = \begin{bmatrix} \cos(kd) & \frac{-\sin(kd)}{E^*k} \\ E^*ksin(kd) & \cos(kd) \end{bmatrix}, \]  

(5.8)

where \( u_L \) and \( u_R \) are displacements at the left and right boundaries of the layer, and \( \sigma_L \) and \( \sigma_R \) are the stresses at the left and right boundaries, \( d \) is the thickness of the layer. TM represents the transfer matrix.

\[ \begin{bmatrix} u_L \\ \sigma_L \end{bmatrix} = \begin{bmatrix} u_{In} + u_{Re} \\ \sigma_{In} + \sigma_{Re} \end{bmatrix} = \begin{bmatrix} (1 + R) \hat{A}_{In} \\ -iE_1k_1(1 - R) \hat{A}_{In} \end{bmatrix}, \]  

(5.9)

\[ \begin{bmatrix} u_R \\ \sigma_R \end{bmatrix} = \begin{bmatrix} u_{Tr} \\ \sigma_{Tr} \end{bmatrix} = \begin{bmatrix} T\hat{A}_{In} \\ -iE_2k_2T\hat{A}_{In} \end{bmatrix}, \]  

(5.10)

where \( \hat{A} \) is the complex amplitude of displacement, the subscripts \( In, Re, \) and \( Tr \) refer to incident, reflected, and transmitted waves, \( k_1 \) and \( k_2 \) are wave number in the incident and transmission bars, and \( E_1 \) and \( E_2 \) are Young’s modulus of the incident and transmission bars( in the ABI experimental setup \( E_1 = E_2 \)), \( R \), and \( T \)
are reflection and transmission amplitude ratios. One can solve for $T$ and $R$, using equations 5.7 to 5.10 as:

$$T = \frac{2}{TM(1, 1) - TM(1, 2)iE_2k_2 - \frac{TM(2, 1)}{iE_1k_1} + \frac{TM(2, 2)E_2k_2}{E_1k_1}},$$  \hspace{1cm} (5.11)

$$R = - [1 - (TM (1, 1) - TM (1, 2) iE_2k_2) T].$$  \hspace{1cm} (5.12)

The transmitted and reflected energy coefficients ($TC$ and $RC$) can be calculated as:

$$TC = |T^2|,$$  \hspace{1cm} (5.13)

$$RC = |R^2|,$$  \hspace{1cm} (5.14)

For long wave lengths (wave length larger than the sample length), multiple reflections of the acoustic wave in the sample could lead to error in attenuation measurement when PS analysis is performed. TM calculation can be used to improve and validate the measured attenuation since it takes into account the multiple reflections between interfaces.

Consider a testing temperature, at a given frequency with a known sample length, the corresponding average wave speed calculated from PS analysis and a guessed attenuation are used to calculate $R$ and $T$ (5.11 and 5.12), where the relation $c = \omega/k$, and Eq. 5.3-5.6 are used. TC and RC (5.13 and 5.14) are also calculated. By minimizing the error between the experimentally-measured transmission coefficient and reflection coefficient ($TC_{EXP}$ and $RC_{EXP}$) and the transfer-matrix-calculated
transmission coefficient and reflection coefficient ($TC_{CAL}$ and $RC_{CAL}$) using the following equation:

$$\text{Error}(f) = \left(\frac{TC_{\text{EXP}}(f) - TC_{CAL}(f)}{TC_{\text{EXP}}(f)}\right)^2 + \left(\frac{RC_{\text{EXP}}(f) - RC_{CAL}(f)}{RC_{\text{EXP}}(f)}\right)^2,$$

(5.15)

the optimized attenuation are obtained for the given frequency and sample length.

5.7 Results and discussions

5.7.1 A comparison between phase spectral analysis (PS) and transfer matrix (TM) method

The reliable frequency range for the current test setup is 5 to 10 kHz for polyurea samples, since below 5 kHz, wavelength is longer than the length of aluminum bar, and above 10 kHz, polyurea is too dissipative for measuring a reliable transmitted signal for the length of polyurea samples.

Fig. 5.13 (a) and 5.13 (b) are $E'$ and $E''$ calculated from PS analysis, shown as functions of frequency. Fig. 5.13 (c) and (d) are $E'$ and $E''$ calculated from the combined PS-TM method. The reason to name it as PS-TM combined method is because the wave speed is calculated from the PS analysis while the attenuation is optimized using TM method. Comparing Fig. 5.13 (b) and (d), it shows that at the two lowest temperatures the drop in the loss modulus in Fig. 5.13(b) is corrected by TM method in Fig. 5.13 (d).

5.14 (a) and (b) are the attenuation calculated from the PS analysis and TM
optimization. For the 10 frequency points between 5 - 10 kHz, both sets of the attenuation data show a peak of attenuation at around 270K~280K. Above that, the attenuation decreases faster as a function of frequency in the result of PS analysis comparing to result by TM method. The trend of the attenuation from ABI test will be compared with the trend of attenuation calculated from the DMA data in the next subsection.

5.7.2 A comparison between ABI and DMA data

- Comparison between ABI test and DMA master curves

DMA tests are conducted for each type of material on the three DMA single-cantilever bending samples which are fabricated from the same batch of the ABI samples, and the average of three DMA tests is used to develop master curves using the method discussed in Chapter 3. These master curves represent the estimations of the storage and loss Young’s moduli at the reference temperature, which is chosen to be 0°C, and in a wide frequency range. The DMA single-cantilever bending tests are conducted at 1 Hz, 2 Hz, 5 Hz, 10 Hz and 20 Hz and from −80°C to 50°C with 3°C increments. The Young’s moduli tested by ABI test are shifted using the same time-temperature dependence measured from the DMA data to compare with DMA master curves. Even though DMA test and ABI test are conducted at different frequencies and different temperatures, they are made comparable by time-temperature superposition at the reference temperature 0°C.

For pure polyurea master curves, as shown in Fig. 5.15 (a), the ABI test data are shifted to the reference temperature using the same shifting factor used for developing the DMA master curves. The two constants in the WLF equation for
Figure 5.13: (a) $E'$ with respect to frequency calculated from PS analysis (b) $E''$ with respect to frequency calculated from PS analysis (c) $E'$ with respect to frequency calculated with $c$ from PS analysis and $\alpha$ from TM method (d) $E''$ with respect to frequency calculated with $c$ from PS analysis and $\alpha$ from TM method
pure polyurea (Eq. 3.4) are \( C_1 = 23.124, C_2 = 200.113K \). For PU.20%MG and PU.40%PMB master curves, as shown in Fig. 5.15 (b) and (c), ABI tests are only conducted at 10°C and the data are shifted to the reference temperature to compare with the DMA master curves. For PU.20%MG, \( C_1 = 50.79, C_2 = 377.15K \). For PU.40%PMB, \( C_1 = 42.29, C_2 = 318.75K \).

As can be seen from Fig. 5.15 (a), for pure polyurea, the storage modulus from ABI test agrees very well with the DMA master curves, while the loss modulus from ABI test is higher than the DMA master curve, both for PS and PS-TM analysis.

In Fig. 5.15 (b) and (c), the storage and loss Young’s moduli of PU.20%MG and PU.40%PMB from ABI test are also compared with the DMA master curves at reference temperature 0°C. Similar to pure polyurea, the ABI test of the composites measures a higher loss modulus comparing to the estimation by DMA master curves.

The reason of the higher loss modulus in the ABI test could due to combined causes, since ABI and DMA are completely different tests and sample deformations are quite different in these tests. From the ABI finite element simulation, we can...
tell that the radial reflection could be one cause of the higher energy loss. Thinner aluminum and sample bars could reduce the influence of the radial deformation. However, considering these completely different tests at different temperatures and different frequencies, these tests data still give a reliable range of the viscoelastic moduli of polyurea and polyurea composites, especially for the storage modulus.

- Comparison of the attenuation between ABI test and DMA test

Even though DMA tests is conducted at much lower frequencies than ABI test, and the sample deformation in the DMA test is different from the deformation in the wave propagation in a bar, it is still meaningful to compare the trend of the attenuation calculated form DMA test to that of ABI test, since it helps to understand the physical meaning of the trend of the attenuation curves in the ABI test.

The attenuation can be calculated from the DMA data by the following equations, which are derived from Eq. 5.3, 5.4 and 5.5, where $\tan\delta = \frac{E''}{E'}$.

$$r = \frac{-1 + \sqrt{1 + \tan^2\delta}}{\tan\delta}$$ (5.16)

$$c = \sqrt{\frac{E'(1 + r^2)}{\rho(1 - r^2)}}$$ (5.17)

Attenuation $\alpha$ can be calculated using $r$ and $c$:

$$\alpha = \frac{-2c\omega + \sqrt{4c^2\omega^2 + 4c^2\tan^2\delta\omega^2}}{2c^2\tan\delta}$$ (5.18)

The attenuation curves of pure polyurea between -80°C to 50 °C, at 1 Hz, 2 Hz, 5 Hz, 10 Hz and 20 Hz are shown in Fig. 5.16. It should be noted that Eq. 5.3,
Figure 5.15: ABI test result comparing with DMA master curves for (a) pure polyurea (PU-P1000) (b) PU 20%MG, and (c) PU 40%PMB. All data shifted to 0°C using time-temperature superposition.
5.4 and 5.5 are derived from wave propagation while DMA single cantilever bending test is a very different measurement technique. The comparison of Fig. 5.14 and Fig. 5.16 shows that the trend of the attenuation calculated from the DMA data is in consistent with the attenuation measured by the ABI test.

The consistency in the trend of the attenuation is important, since it helps us to understand what each part of the attenuation curve means. The peaks of the DMA attenuation curves are located approximately at the same temperature as its peak of $\tan\delta$, which is related with the glass transition. The time-temperature superposition of polymers suggests that higher temperature is equivalent to lower frequency and lower temperature is equivalent to higher frequency in terms of the polymer behavior. DMA test is conducted at a lower frequency than ABI test. Suppose the frequency of DMA test, $\omega_{DMA}$, is in the order of $10^1$, and the frequency of ABI test, $\omega_{ABI}$, is in the order of $10^3$. The equivalent temperature change between the two test frequencies can be calculated from the following equations:

$$\omega_{DMA} = a(T_{ABI}, T_{DMA}) \omega_{ABI}$$

$$\log(a(T_{ABI}, T_{DMA})) = -3 = \frac{-C_1(T_{ABI} - T_{DMA})}{C_2 + (T_{ABI} - T_{DMA})}$$

where $C_1 = 23.124$, $C_2 = 200.113K$ for pure polyurea. We have $T_{ABI} - T_{DMA} = 29.8K$, which is approximately the difference in the peak location comparing Fig. 5.14 and Fig. 5.16.

From the comparison of the trend of the attenuation between ABI test and DMA master curves, we conclude that in the ABI test, below 270°280K, polyurea
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Figure 5.16: Attenuation of pure polyurea (PU-P1000) calculated from DMA data (-80°C-50°C) .

behaves stiff and glassy. It explains the completely different trends below and above 270°C-280K in Fig. 5.14.

5.8 Conclusion of ABI test

A novel characterization technique, ABI test, has been developed to directly measure the viscoelastic properties of polyurea and its composite materials at the mid-level (kHz) frequencies, which fills the gap between the dynamic mechanical analysis and the ultrasonic wave measurement.

The comparison of the ABI and DMA results in the form of the master curves shows that the storage modulus matches remarkably well for the two tests while the loss modulus from the ABI test is higher than the DMA master curves. The reason of the difference in the loss modulus could be related with the radial reflections in the sample. Further research could be conducted changing the diameter of the aluminum
and sample bars.

Regardless of the higher loss modulus, it is still a successful experimental work in terms of making direct measurement at this challenging frequency range and obtaining the storage modulus that matches well with the DMA master curves. This characterization technique is not limited to polyurea and its composites. It can also be applied for other similar viscoelastic materials.

This chapter, in part, appears in the paper A Novel Characterization Technique for Viscoelastic Properties of Polyurea at Mid-level (kHz) Frequencies, which is in preparation by W. Nantasetphong, Z. Jia, A. V. Amirkhizi, and S. Nemat-Nasser.

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Bibliography


[74] Inc. ultran laboratories. Modern ultrasonic transducers including phenomenally high sensitivity and high frequency non-contact transducers.


Appendix A

Error analysis for DMA

shear-sandwich test of polyurea

TA 2980 has a shear-sandwich test grip, as shown in Fig. A.1. Two thin polymer samples could be placed in the two slots between the fixed and movable grips.

Implicit finite element simulations are conducted on LS-DYNA to estimate the error of DMA shear testing for polyurea samples of various thicknesses using this shear-sandwich test grip. The shear-sandwich test requires two identical pieces of sample, but due to symmetry, only one sample is simulated. In the simulation, the size of the surface in contact with the grip is set to be $2mm \times 2mm$, which is calculated based on the load capacity of TA2980, which is 20N. Elastic material model is used for polyurea, assuming that the shear modulus of polyurea is 33.78 MPa, and the Poisson’s ratio is 0.48. The convergence test has been conducted to make sure the mesh is fine enough. A picture of the model is shown in Fig. A.2. The shear modulus is calculated as:
\[ \mu = \left( \frac{F}{A} \right) / \left( \frac{u_y}{t} \right) = \frac{F t}{A u_y} \]  

(A.1)

This calculated shear modulus from Eq. A.1 is compared with the nominal shear modulus, and the error \( e = \frac{\mu - \mu_0}{\mu_0} \) is shown in Fig. A.3. The sample surfaces that are perpendicular to the contacting surfaces are the free surfaces, the larger the free surface, the larger the errors are for measuring shear modulus. This is why when the thickness of the sample is very small, the FEA measured shear modulus converges to the nominal shear modulus. But in the real experiment, when the polyurea sample is very thin, much larger force is needed for the sample to have a measurable displacement, which would exceed the maximum load of TA 2980. Thus shear sandwich DMA test is better applicable for thin softer materials [14], and polyurea is too stiff for the shear sandwich test on TA2980.

It should be noted that this difference between the FEA measured shear modulus and the nominal shear modulus is not only a function of the sample thickness, for example, it is also affected by the sample stiffness and Poisson’s ratio. Thus most
Figure A.2: Finite element model for the DMA shear test. Only one of the two identical samples is simulated.

of the DMA test for polyurea and polyurea composites are tested by single cantilever bending or tension test.
Figure A.3: Simulation result: the error of the DMA shear-sandwich test comparing to the real shear modulus of the sample.
Appendix B

Derivation of Kramers-Kronig relations for relaxation modulus and creep compliance

B.1 Kramers-Kronig relations for relaxation modulus

Start from the definition of Fourier transform:

\[ F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(t)e^{-i\omega t} dt \]

If \( f(t) \) is a finite real causal function, which means \( f(\tau) = 0 \) for \( \tau < 0 \), thus Fourier transform reduces to:

\[ F(\omega) = \frac{1}{2\pi} \int_{0}^{\infty} f(t)e^{-i\omega t} dt \]
If frequency is complex, i.e. $\omega = \omega_r + i\omega_i$, then

$$F(\omega) = \frac{1}{2\pi} \int_0^\infty f(t)e^{-i(\omega_r + i\omega_i)t}dt = \frac{1}{2\pi} \int_0^\infty f(t)e^{-i\omega_r t}e^{\omega_i t}dt$$

This integral converges only when $\omega_i < 0$. Thus $F(\omega)$ is analytic on the lower-half complex plane.

Viscoelastic constitutive relation can be written as:

$$\sigma(t) = \int_{-\infty}^t G(t-\tau)\dot{\epsilon}(\tau)d\tau = \int_0^\infty G(\tau)\dot{\epsilon}(t-\tau)d\tau$$

where $G(\tau)$ is causal ($G(\tau) = 0$ when $\tau < 0$), which means that an output at time $t$ is obtained only due to inputs at or before $t$.

Since $G(\omega)$ is analytic in the lower-half plane, integrand $\frac{G(\omega)}{\omega-u}$ is also analytic in the lower-half plane, where $u$ is real. Take the contour integral as follows:

Figure B.1: Integral contour in the lower-half plane which includes two half circles $C_1$ and two straight lines.

For contour $C_1$, $\omega = Re^{i\theta}$, $d\omega = Rie^{i\theta}d\theta$, then
\[
\int_{C_1} \frac{G(\omega)}{\omega - u} d\omega = \int_{-\pi}^{0} \frac{G(\omega)}{Re^{i\theta} - u} Re^{i\theta} d\theta
\]

when \( R \to \infty \)

\[
= \int_{-\pi}^{0} \frac{G(\infty)}{Re^{i\theta}} Re^{i\theta} d\theta = G(\infty)i\pi
\]

For contour \( C_2 \), \( \omega = \rho e^{i\theta} + u \), \( d\omega = \rho ie^{i\theta} d\theta \), then

\[
\int_{C_2} \frac{G(\omega)}{\omega - u} d\omega = \int_{0}^{-\pi} \frac{G(\omega)}{\rho e^{i\theta} + u - u} \rho ie^{i\theta} d\theta = \int_{0}^{-\pi} \frac{G(\omega)}{\rho e^{i\theta}} \rho ie^{i\theta} d\theta
\]

when \( \rho \to 0 \)

\[
= -G(u)i\pi
\]

For contour \( C_3 \)

\[
\int_{C_3} \frac{G(\omega)}{\omega - u} d\omega = C.P. \int_{-\infty}^{\infty} \frac{G(\omega)}{\omega - u} d\omega = -C.P. \int_{-\infty}^{\infty} \frac{G(\omega)}{\omega - u} d\omega
\]

where C.P. stands for Cauchy principal value, and \( \omega \) is real.

As the integrand is analytic inside the closed contour, we have

\[
\int_{C_1} \frac{G(\omega)}{\omega - u} d\omega + \int_{C_2} \frac{G(\omega)}{\omega - u} d\omega + \int_{C_3} \frac{G(\omega)}{\omega - u} d\omega = 0
\]

substitute in the integral results for contours \( C_1 \) and \( C_2 \) and \( C_3 \):
G(∞)iπ - G(u)iπ - C.P. \int_{-\infty}^{\infty} \frac{G(\omega)}{\omega - u} d\omega = 0

G(u) - G(\infty) = -\frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{G(\omega)}{\omega - u} d\omega \quad (B.1)

Separating the real and imaginary parts of the function G(u), we get

G'(u) + iG''(u) - G(\infty) = -\frac{1}{i\pi} C.P. \int_{-\infty}^{\infty} \frac{G''(\omega) + iG'''(\omega)}{\omega - u} d\omega

G'(u) - G(\infty) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{G''(\omega)}{\omega - u} d\omega \quad (B.2)

G'''(u) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{G'(\omega)}{\omega - u} d\omega \quad (B.3)

where G(\infty) is real, and the integrals stand for Cauchy principal value.

Since G(t) is real, the real part of its Fourier transform is an even function and the imaginary part of its Fourier transform is an odd function. Eq. (B.2) and (B.3) can be reduced to:

G'(u) - G(\infty) = -\frac{1}{\pi} \int_{-\infty}^{0} \frac{G''(\omega)}{\omega - u} d\omega - \frac{1}{\pi} \int_{0}^{\infty} \frac{G''(\omega)}{\omega - u} d\omega

= -\frac{1}{\pi} \int_{0}^{\infty} \frac{G''(-\omega)}{-\omega - u} d(-\omega) - \frac{1}{\pi} \int_{0}^{\infty} \frac{G''(\omega)}{\omega - u} d\omega
\[
G''(u) = \frac{1}{\pi} \int_{-\infty}^{0} \frac{G'(\omega)}{\omega - u} d\omega + \frac{1}{\pi} \int_{0}^{\infty} \frac{G'(\omega)}{\omega - u} d\omega
\]

\[
= \frac{1}{\pi} \int_{\infty}^{0} \frac{G'(-\omega)}{-\omega - u} d(-\omega) + \frac{1}{\pi} \int_{0}^{\infty} \frac{G'(\omega)}{\omega - u} d\omega
\]

\[
= \frac{1}{\pi} \int_{0}^{\infty} \frac{G'(-\omega)}{\omega + u} d\omega + \frac{1}{\pi} \int_{\infty}^{0} \frac{G'(\omega)}{\omega - u} d\omega
\]

\[
= \frac{1}{\pi} \int_{0}^{\infty} \frac{G'(\omega)}{\omega + u} d\omega + \frac{1}{\pi} \int_{0}^{\infty} \frac{G'(\omega)}{\omega - u} d\omega
\]

\[
= \frac{2u}{\pi} \int_{0}^{\infty} \frac{G'(\omega)}{\omega^2 - u^2} d\omega
\]  

Eq. (B.4) and Eq.(B.5) are the Kramers-Kronig relations for the relaxation modulus.
B.2 Kramers-Kronig relations for creep compliance

The difference between the expression of the frequency-domain relaxation modulus and creep compliance is the sign of the imaginary part.

\[ G^*(\omega) = G'(\omega) + iG''(\omega) \]

\[ J^*(\omega) = J'(\omega) - iJ''(\omega) \]

The imaginary part of the relaxation modulus is positive and the imaginary part of the creep compliance is negative, because the viscosity of the material must dissipate energy but not generate energy.

The derivation of the Kramers-Kronig relations for creep compliance is generally the same as relaxation modulus up to Eq. (B.1). Then substitute \( J^*(\omega) = J'(\omega) - iJ''(\omega) \) into the integrand and get:

\[ J'(u) - iJ''(u) - J(\infty) = -\frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{J'(\omega) - iJ''(\omega)}{\omega - u} d\omega \]

\[ J'(u) - J(\infty) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{J''(\omega)}{\omega - u} d\omega \]

\[ J''(u) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{J'(\omega)}{\omega - u} d\omega \]
which have a sign difference comparing to the Kramers-Kronig relations for the relaxation modulus (Eq. B.2 and B.3).

The final form of the Kramers-Kronig relations for the creep relaxation are:

\[
J'(u) - J(\infty) = \frac{2}{\pi} \int_0^\infty \frac{\omega J''(\omega)}{\omega^2 - u^2} d\omega
\]  
(B.6)

\[
J''(u) = -\frac{2u}{\pi} \int_0^\infty \frac{J'(\omega)}{\omega^2 - u^2} d\omega
\]  
(B.7)

Eq. (B.6) and (B.7) are the same as in [49]. In their paper, the Kramers-Kronig relations are for bulk compliance.

### B.3 Integration of the Kramers-Kronig relations for relaxation modulus

In order to calculate the integral in Eq. (B.2), (B.3), (B.6) and (B.7), experimental data needs to be extended as piece-wise linear functions. \([\omega_1, \omega_2, ..., \omega_n]\) and \([G^*_1, G^*_2, ..., G^*_n]\) are the x and y data points of the experimental master curves. \([\Omega_0, \Omega_1, ..., \Omega_{n+2}]\) and \([\bar{G}^*_0, \bar{G}^*_1, ..., \bar{G}^*_n]\) are the new x and y data points of the extended master curves in \([0, \infty)\), where \(\bar{G}^*_i = \overline{G}'_i + i\overline{G}''_i\). This extension is based on the method in [61], but the extension in the loss modulus is modified.

The data extension is as follows:

\[
\Omega_0 = 0, \quad \Omega = \frac{\omega_1}{2}, ..., \Omega_n = \frac{\omega_{n-1} + \omega_n}{2}, \quad \Omega_{n+1} = \omega_n + \frac{\omega_n - \omega_{n-1}}{2}, \quad \Omega_{n+2} = +\infty
\]
\[ G'_0 = G'_1, \ G'_1 = G'_2, \ldots, \ G'_n = \frac{G'_{n-1} + G'_{n+1}}{2}, \ G'_{n+1} = G'_n, \ G'_{n+2} = G'_n \]

\[ G''_0 = 0, \ G''_1 = \frac{G''_1}{2}, \ldots, \ G''_n = \frac{G''_{n-1} + G''_{n+1}}{2}, \ G''_{n+1} = 0, \ G''_{n+2} = 0 \]

Each linear segment of storage modulus is approximated as:

\[ G'(u) = a_i \omega + b_i, \ \Omega_i \leq \omega < \Omega_{i+1}, \ i = 0, 1, \ldots, n+1. \]

\[ G''(u) = c_i \omega + d_i, \ \Omega_i \leq \omega < \Omega_{i+1}, \ i = 0, 1, \ldots, n+1. \]

For integrals with \( ax^2 + b \) \((a > 0)\)

\[ \int \frac{x^2}{ax^2 + b} \, dx = \frac{x}{a} - \frac{b}{a} \int \frac{dx}{ax^2 + b} \]

\[ \int \frac{dx}{ax^2 + b} = \frac{1}{2\sqrt{-ab}} \ln \left| \frac{\sqrt{ax} - \sqrt{-b}}{\sqrt{ax} + \sqrt{-b}} \right| + c, \ for \ b < 0 \]

\[ \int \frac{x}{ax^2 + b} \, dx = \frac{1}{2a} \ln |ax^2 + b| + c \]

Then we get
\[
\int_{\Omega_i}^{\Omega_{i+1}} \frac{c_i \omega^2}{\omega^2 - u^2} d\omega = \left. c_i \left( \omega + u^2 \int \frac{d\omega}{\omega^2 - u^2} \right) \right|_{\omega=\Omega_i}^{\omega=\Omega_{i+1}}
\]

\[
= c_i \left( \omega + u^2 \int \frac{d\omega}{2 \sqrt{u^2} \ln \left| \frac{\omega - u}{\omega + u} \right|} + c \right) \bigg|_{\omega=\Omega_i}^{\omega=\Omega_{i+1}}
\]

\[
= c_i (\Omega_{i+1} - \Omega_i) + \left( \frac{c_i u}{2} \ln \left| \frac{\Omega_{i+1} - u}{\Omega_i + u} \right| - \frac{c_i u}{2} \ln \left| \frac{\Omega_i - u}{\Omega_i + u} \right| \right)
\]

\[
= c_i (\Omega_{i+1} - \Omega_i) + \frac{c_i u}{2} \ln \left| \frac{(\Omega_{i+1} - u)(\Omega_i + u)}{(\Omega_i + u)(\Omega_i - u)} \right|
\]

\[
\int_{\Omega_i}^{\Omega_{i+1}} \frac{d_i \omega}{\omega^2 - u^2} d\omega = \left. \frac{d_i}{2} \ln \left| \omega^2 - u^2 \right| \right|_{\omega=\Omega_i}^{\omega=\Omega_{i+1}} = \frac{d_i}{2} \ln \left| \frac{\Omega_{i+1}^2 - u^2}{\Omega_i^2 - u^2} \right|
\]

\[
\int_{\Omega_i}^{\Omega_{i+1}} \frac{a_i \omega}{\omega^2 - u^2} d\omega = \left. \frac{a_i}{2} \ln \left| \omega^2 - u^2 \right| \right|_{\omega=\Omega_i}^{\omega=\Omega_{i+1}} = \frac{a_i}{2} \ln \left| \frac{\Omega_{i+1}^2 - u^2}{\Omega_i^2 - u^2} \right|
\]

\[
\int_{\Omega_i}^{\Omega_{i+1}} \frac{b_i}{\omega^2 - u^2} d\omega = \left. \frac{b_i}{2u} \ln \left| \frac{\omega - u}{\omega + u} \right| + c \right|_{\omega=\Omega_i}^{\omega=\Omega_{i+1}} = \frac{b_i}{2u} \ln \left| \frac{(\Omega_{i+1} - u)(\Omega_i + u)}{(\Omega_i + u)(\Omega_i - u)} \right|
\]

Thus
\[ G'(u) - G(\infty) = -\frac{2}{\pi} \int_0^\infty \frac{\omega G''(\omega)}{\omega^2 - u^2} d\omega \]

\[ = -\frac{2}{\pi} \int_{\Omega_0}^{\Omega_1} \frac{\omega(c_0\omega + d_0)}{\omega^2 - u^2} d\omega - \frac{2}{\pi} \int_{\Omega_1}^{\Omega_2} \frac{\omega(c_1\omega + d_1)}{\omega^2 - u^2} d\omega - \cdots \]

\[ -\frac{2}{\pi} \int_{\Omega_n}^{\Omega_{n+1}} \frac{\omega(c_n\omega + d_n)}{\omega^2 - u^2} d\omega - \frac{2}{\pi} \int_{\Omega_{n+1}}^{\Omega_{n+2}} \frac{\omega(c_{n+1}\omega + d_{n+1})}{\omega^2 - u^2} d\omega \]

\[ = -\frac{2c_0}{\pi} \Omega_1 - \frac{\omega c_0}{\pi} ln \left| \frac{\Omega_1 - u}{\Omega_1 - u} \right| \]

\[ -\frac{2}{\pi} \sum_{i=1}^{n} \left[ c_i(\Omega_{i+1} - \Omega_i) + \frac{\omega c_i}{2} ln \left| \frac{(\Omega_{i+1} - u)(\Omega_i + u)}{(\Omega_{i+1} + u)(\Omega_i - u)} \right| + \frac{d_i}{2} ln \left| \frac{\Omega_i^2 - u^2}{\Omega_i^2 - u^2} \right| \right] \]

(In the calculation, \(d_{n+1}\) must equal to zero, otherwise the integral for the last segment \([\Omega_{n+1}, \Omega_{n+2}]\) does not converge, and \(c_{n+1}\) must equal to zero too, otherwise loss modulus goes to infinity when frequency goes to infinity, which is not physical.)

\[ G''(u) = \frac{2}{\pi} \int_0^\infty \frac{u G'(\omega)}{\omega^2 - u^2} d\omega = \frac{2u}{\pi} \int_{\Omega_0}^{\Omega_1} \frac{a_0\omega + b_0}{\omega^2 - u^2} d\omega + \frac{2u}{\pi} \int_{\Omega_1}^{\Omega_2} \frac{a_1\omega + b_1}{\omega^2 - u^2} d\omega + \cdots \]

\[ + \frac{2u}{\pi} \int_{\Omega_n}^{\Omega_{n+1}} \frac{a_n\omega + b_n}{\omega^2 - u^2} d\omega + \frac{2u}{\pi} \int_{\Omega_{n+1}}^{\Omega_{n+2}} \frac{a_{n+1}\omega + b_{n+2}}{\omega^2 - u^2} d\omega \]
\[ \frac{b_0}{\pi} \ln \left| \frac{\Omega_1 - u}{\Omega_1 + u} \right| + \sum_{i=1}^{n} \left[ \frac{\omega a_i}{\pi} \ln \left| \frac{\Omega_{i+1}^2 - u^2}{\Omega_i^2 - u^2} \right| + \frac{b_i}{\pi} \ln \left| \frac{(\Omega_{i+1} - u)(\Omega_i + u)}{(\Omega_{i+1} - u)(\Omega_i - u)} \right| \right] \]

\[ + \frac{b_{n+1}}{\pi} \ln \left| \frac{\Omega_{n+1} + u}{\Omega_{n+1} - u} \right| \]

These integration results are the same as in [61].

**B.4 Integration of the Kramers-Kronig relations for creep compliance**

For creep compliance, if similar piece-wise linear extension is used, the integrations of the Kramers-Kronig relations are equal to:

\[ J'(u) - J(\infty) = \frac{2}{\pi} \int_{0}^{\infty} \frac{\omega J''(\omega)}{\omega^2 - u^2} d\omega \]

\[ = \frac{2}{\pi} \int_{0}^{\Omega_1} \frac{\omega(c_0\omega + d_0)}{\omega^2 - u^2} d\omega + \frac{2}{\pi} \int_{\Omega_1}^{\Omega_2} \frac{\omega(c_1\omega + d_1)}{\omega^2 - u^2} d\omega + ... \]

\[ + \frac{2}{\pi} \int_{\Omega_n}^{\Omega_{n+1}} \frac{\omega(c_n\omega + d_n)}{\omega^2 - u^2} d\omega + \frac{2}{\pi} \int_{\Omega_{n+1}}^{\Omega_{n+2}} \frac{\omega(c_{n+1}\omega + d_{n+1})}{\omega^2 - u^2} d\omega \]
\[ J''(u) = -\frac{2}{\pi} \int_0^\infty \frac{u J'(\omega)}{\omega^2 - u^2} d\omega \]

\[ = -\frac{2}{\pi} \int_{\Omega_0}^{\Omega_1} \frac{a_0 \omega + b_0}{\omega^2 - u^2} d\omega - \frac{2}{\pi} \int_{\Omega_1}^{\Omega_2} \frac{a_1 \omega + b_1}{\omega^2 - u^2} d\omega - \ldots \]

\[ = -\frac{2}{\pi} \int_{\Omega_n}^{\Omega_{n+1}} \frac{a_n \omega + b_n}{\omega^2 - u^2} d\omega - \frac{2}{\pi} \int_{\Omega_{n+1}}^{\Omega_{n+2}} \frac{a_{n+1} \omega + b_{n+2}}{\omega^2 - u^2} d\omega \]

\[ = -\frac{b_0}{\pi} \ln \frac{\Omega_1 - u}{\Omega_1 + u} - \sum_{i=1}^{n} \left[ \frac{\omega a_i}{\pi} \ln \frac{\Omega_{i+1}^2 - u^2}{\Omega_i^2 - u^2} + \frac{b_i}{\pi} \ln \frac{(\Omega_{i+1} - u)(\Omega_i + u)}{(\Omega_{i+1} + u)(\Omega_i - u)} \right] \]

\[ -\frac{b_{n+1}}{\pi} \ln \frac{\Omega_{n+1} + u}{\Omega_{n+1} - u} \]
Appendix C

Glass mold surface treatment

Silane surface treatment can be applied on the glass surface to make nonstick glass molds for polyurea sample fabrication. The flatness and smoothness of the glass surface is usually better than the machined surface of Teflon molds. The transparency of the glass also makes it easy to monitor the casting process. Fig. C.2 is showing the fabrication of large polyurea thin film using the nonstick glass plates.

The surface treatment of nonstick glass plates can use trimethoxy(octyl)silane discussed in Chapter 4 or use dichlorodimethylsilane (Fig. C.1). Different from trimethoxy(octyl)silane, dichlorodimethylsilane needs dry environment to graft on the glass surface.

\[
\text{CH}_3 \quad \text{Cl} \quad \text{Si} \quad \text{CH}_3 \quad \text{Cl}
\]

Figure C.1: Molecular structure of dichlorodimethylsilane, which creates a highly non-polar surface.
Figure C.2: Polyurea thin film casting using the surface-treated nonstick glass mold.

The procedure of surface treatment of glass plates using dichlorodimethylsilane:

1. Clean glass surface with soap and rinse thoroughly with deionized water
2. Completely dry glass molds in the oven at 110°C for 1 hour
3. Take out the dried glass plates and cool to room temperature
4. Apply dichlorodimethylsilane on the glass surface for at least 2-3 minutes
5. Rinse off the extra dichlorodimethylsilane by ethanol
6. Cure the treated glass surface in 110°C oven for 1 hour
7. This treated glass surface can be cleaned by ethanol and paper towels after every use and reused for many times. Avoid scraping or scratching the surface.

* Pure dichlorodimethylsilane is very volatile and will strongly irritate skin, so it needs to be handled very carefully.

* The surface treated glass surface should be quite hydrophobic and nonstick to regular tapes. Check the surface with tapes before casting samples.