INVESTIGATION OF SINGLE AND DOUBLE NETWORK GELS BY
MAXIMUM BUBBLE PRESSURE RHEOLOGY

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INVESTIGATION OF SINGLE AND DOUBLE NETWORK GELS BY

MAXIMUM BUBBLE PRESSURE RHEOLOGY

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ABSTRACT

Double-network gels have gained more and more concern of gel scientists due to its interesting physical behaviors when compared with traditional single-network gels. In this research, Poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer was mixed together with 12-hydroxystearic acid (12-HSA) and mineral oil (M.O.) to construct a gel, which contains two three dimensional networks generated by the two gelators. At the same time, mineral oil was mixed with poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer and 12-hydroxystearic acid (12-HSA) respectively to prepare two single-network gels, which were used in the comparative experiments. Gel samples prepared were used in maximum bubble pressure measurements in order to characterize the basic rheological properties of the gel samples, and compared to oscillatory shear rheological measurements. Results obtained from the two series of measurements are compared in order to find out the changes in rheological properties that the additive of 12-HSA brings to the two-network gel system.

The maximum bubble pressure method was studied and demonstrated as an effective method to characterize rheological properties of gels. Dibenzylidene Sorbitol/polyethylene glycol 400 (DBS/PEG 400) gel samples and dimethyldibenzylidene sorbitol/polyethylene glycol 400 (DMDBS/PEG 400) gel samples were prepared and were used in maximum bubble pressure measurements.
The gel transition temperatures were measured by both maximum bubble pressure method and tilting tests, and results obtained from experiments above were compared and discussed.
ACKNOWLEDGMENTS

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Finally, I want to dedicate this thesis to my beloved parents, I won’t have gone so far without their selfless love!
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES ......................................................................................................................... ix</td>
</tr>
<tr>
<td>LIST OF FIGURES .......................................................................................................................... x</td>
</tr>
</tbody>
</table>

## CHAPTER

### Ⅰ. INTRODUCTION .................................................................................................................. 1

### Ⅱ. BACKGROUND ...................................................................................................................... 3

#### 2.1 Introduction to gels ....................................................................................................... 3

- 2.1.1 Definition of a gel ........................................................................................................ 3
- 2.1.2 Categories of gels ........................................................................................................ 3
- 2.1.3 Applications of gels ....................................................................................................... 4

#### 2.2 Introduction to double-network gels ........................................................................... 5

#### 2.3 Maximum bubble pressure method ............................................................................. 7

- 2.3.1 Introduction of maximum bubble pressure method ................................................... 7
- 2.3.2 Maximum bubble pressure rheology in characterization of gel properties ................. 9

#### 2.4 Introduction to gelators and the solvents ................................................................. 11

- 2.4.1 Dibenzylidene sorbitol and dimethyldibenzylidene sorbitol gelator ....................... 11
- 2.4.2 12-hydroxystearic acid gelator ............................................................................... 12
- 2.4.3 Poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) gelator ..................... 13
- 2.4.4 Network dispersed in double-network gel ............................................................... 14
III. EXPERIMENTAL METHODS ................................................................. 15
  3.1 Materials ......................................................................................... 15
    3.1.1 Chemicals used as received ....................................................... 15
    3.1.2 Chemicals used after purification ............................................. 15
  3.2 Preparation of gels ......................................................................... 16
  3.3 Preparation of samples for rheological tests ...................................... 17
  3.4 Characterization methods ................................................................. 18
    3.4.1 Tilting tests ................................................................................ 19
    3.4.2 Maximum bubble pressure rheology measurements .................. 20
    3.4.3 Rheological tests for SEBS/M.O. gel and the double-network gel .... 21
IV. RESULTS AND DISCUSSIONS .............................................................. 22
  4.1 Gel transition temperature measured by tilting tests and maximum bubble pressure method ........................................................................................................... 22
    4.1.1 Characterization of DBS/PEG 400 gel transition temperature ....... 22
      4.1.1.1 DBS/PEG 400 gel transition temperature characterized by tilting test ......................................................................................................................... 22
      4.1.1.2 DBS/PEG 400 gel transition temperature characterized by maximum bubble pressure method ................................................................. 23
    4.1.2 Characterization of DMDBS/PEG 400 gel transition temperature ...... 24
      4.1.2.1 DMDBS/PEG 400 gel transition temperature characterized by tilting test ........................................................................................................... 25
      4.1.2.2 DMDBS/PEG 400 gel transition temperature characterized by maximum bubble pressure method ................................................................. 26
  4.2 Study of the double-network gel ........................................................ 27
    4.2.1 Preparation of gels ...................................................................... 28
    4.2.2 Maximum bubble pressure measurements .................................... 29
4.2.2.1 Maximum bubble pressure measurement on 12-HSA/M.O. gel. 30
4.2.2.2 Maximum bubble pressure measurement on SEBS/M.O. gel.....31
4.2.2.3 Maximum bubble pressure measurement on the double-network gels........................................................................................................... 32

4.2.3 Rheological tests.................................................................................. 36
4.2.3.1 Rheological tests for 10% SEBS/M.O. gel................................. 36
4.2.3.2 Rheological tests for the 10% blend..............................................44

V. CONCLUSION.................................................................................................................51

REFERENCES.......................................................................................................................52
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3- 1 Mass fractions of components in 12-HSA+SEBS/M.O. gel</td>
<td>17</td>
</tr>
<tr>
<td>3- 2 Mass fractions of components in SEBS/M.O. gels</td>
<td>17</td>
</tr>
<tr>
<td>3- 3 Mass fractions of components in 12-HSA/M.O. gels</td>
<td>17</td>
</tr>
<tr>
<td>3- 4 Components of maximum bubble pressure apparatus</td>
<td>20</td>
</tr>
<tr>
<td>4- 1 Gel transition temperature measured by tilting test and MBPM</td>
<td>27</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Barbituric acid and pyrimidine units bonded with each other in solvent thus generates a two component network to form a gel</td>
</tr>
<tr>
<td>2-2</td>
<td>Variation of bubble shape and pressure change in the bubble</td>
</tr>
<tr>
<td>2-3</td>
<td>Illustration of devices used in the maximum bubble pressure measurements</td>
</tr>
<tr>
<td>2-4</td>
<td>Chemical structure of dibenzylidene sorbitol</td>
</tr>
<tr>
<td>2-5</td>
<td>Chemical structure of dimethyldibenzylidene sorbitol</td>
</tr>
<tr>
<td>2-6</td>
<td>Chemical structure of 12-hydroxystearic acid</td>
</tr>
<tr>
<td>2-7</td>
<td>Schematic diagram of stereochemistry of 12-hydroxystearic acid</td>
</tr>
<tr>
<td>2-8</td>
<td>Chemical structure of Poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer</td>
</tr>
<tr>
<td>2-9</td>
<td>Poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer and 12-hydroxystearic acid dispersed in mineral oil</td>
</tr>
<tr>
<td>3-1</td>
<td>Process of preparing disk like samples for rheological tests</td>
</tr>
<tr>
<td>4-1</td>
<td>DBS gels tilted to 90 degree angle during tilting tests</td>
</tr>
<tr>
<td>4-2</td>
<td>Maximum pressure plotted as a function of temperature</td>
</tr>
<tr>
<td>4-3</td>
<td>DMDBS gels tilted to 90 degree angle during tilting tests</td>
</tr>
<tr>
<td>4-4</td>
<td>Maximum pressure plotted as a function of temperature</td>
</tr>
<tr>
<td>4-5</td>
<td>Appearance of SEBS/M.O. gel samples with different concentrations</td>
</tr>
<tr>
<td>4-6</td>
<td>Appearance of 12-HSA+SEBS/M.O. gel samples with different concentrations</td>
</tr>
<tr>
<td>4-7</td>
<td>Plots of maximum bubble pressure versus temperature for 1% 12-HSA/M.O. gel</td>
</tr>
</tbody>
</table>
4- 8 Plots of maximum bubble pressure versus temperature for 5%, 10% and 15% SEBS/M.O. gel.......................................................... 31
4- 9 Plots of maximum bubble pressure versus temperature for 5%, 10% and 15% double-network gels.......................................................... 32
4- 10 Plots of $P_{\text{MAX}}$ (double-network gel), $P_{\text{MAX}}$ (12-HSA) +$P_{\text{MAX}}$ (SEBS) versus temperature for 5%, 10% and 15% gels.......................................................... 34
4- 11 Plots of $P_{\text{MAX}}$ (blend)/ ($P_{\text{MAX}}$ (12-HSA) +$P_{\text{MAX}}$ (SEBS)) versus temperature for 5%, 10% and 15% gels.......................................................... 35
4- 12 Plots of storage modulus $G'$ and loss modulus $G''$ versus strain amplitude for 10% SEBS/M.O. gel at two temperatures. $G'$, 50°C (■), 80°C (▲); $G''$, 50°C (●), 80°C (▼) .......................................................... 36
4- 13 Plots of storage modulus $G'$ and loss modulus $G''$ versus temperature for 10% SEBS/M.O. gel.......................................................... 38
4- 14 Plots of tan (delta) versus temperature for 10% SEBS/M.O. gel.......................... 38
4- 15 Plots of oscillation torque versus frequency for 10% SEBS/M.O. gel at seven temperatures. The dash-dot line indicates the minimum torque limit of the machine. .......................................................... 40
4- 16 Plots of storage modulus $G'$ versus frequency for 10% SEBS/M.O. gel at seven temperatures.......................................................... 41
4- 17 Plots of loss modulus $G''$ versus frequency for 10% SEBS/M.O. gel at seven temperatures.......................................................... 41
4- 18 Plots of tan (delta) versus frequency for 10% SEBS/M.O. gel at seven temperatures.......................................................... 43
4- 19 Plots of storage modulus $G'$ and loss modulus $G''$ versus strain amplitude for the 10% blend at two temperatures. $G'$, 50°C (■), 80°C (▲), $G''$, 50°C (●), 80°C (▼). 44
4- 20 Plots of storage modulus $G'$ and loss modulus $G''$ versus temperature for the 10% blend.......................................................... 45
4- 21 Plots of tan (delta) versus temperature for the 10% blend........................................ 46
4- 22 Plots of oscillation torque versus frequency for the 10% blend at seven temperatures. The dash-dot line indicates the minimum torque limit of the machine. .................................................................................... 48
4- 23 Plots of storage modulus $G'$ versus frequency for the 10% blend at seven temperatures.......................................................... 49
4- 24 Plots of loss modulus $G''$ versus frequency for the 10% blend at seven temperatures.............................................................................. 49
4-25 Plots of tan (delta) versus frequency for the 10% blend at nine temperatures... 50
A gel system that contains two networks (i.e. double-network gel) has been of interest to scientists’ in recent years\textsuperscript{16-18}. A micro quantity additive of another gelator in a gel could bring significant changes to the gel’s physical properties. The main goal of the research is to study the changes of physical behaviors when a second gelator is added into an existing single-network gel. In this research, a double-network gel system was prepared to carry out measurements to characterize the physical properties of this unique system. Poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer and 12-hydroxystearic acid were used as the two gelators which were mixed together with mineral oil to construct this new gel. And two single-network gels using the SEBS block copolymer and the 12-HSA as gelators were prepared to be used in the comparative experiments. The properties of the three gels are characterized by using traditional rheological measurements and the maximum bubble pressure method tests, and the advantages and disadvantages of maximum bubble pressure method is discussed in this thesis.

In terms of a gel, one of the most important properties, $T_{gel}$, the temperature when the system transits from solid state to liquid state, is the key point to study how a gel behaves under different thermal environments\textsuperscript{1-3}. Usually $T_{gel}$ depends on the concentration of the gelator, type of the solvent and the preparation procedure of the
solution cooling step. $T_{gel}$ could be characterized in several methods reported by scientists over time, such as tube tilting method, falling ball method, bubble rise method and oscillatory shear method. A method called the maximum bubble pressure method has been of interest in recent years. The method was first proposed by Simon to measure the surface tension of liquids with surfactants in 1851, and it has been developed afterwards to measure the local modulus of soft materials by Crosby and his co-workers. In this research, dibenzylidene Sorbitol/polyethylene glycol 400 (DBS/PEG 400) gel samples and dimethyldibenzylidene sorbitol/polyethylene glycol 400 (DMDBS/PEG 400) gel samples were prepared and the gel transition temperature was measured by using the maximum bubble pressure method and tilting test. And results are put together to be compared with each other to discuss the advantages and disadvantages of maximum bubble pressure method.
CHAPTER Ⅱ

BACKGROUND

2.1 Introduction to gels

Researches about gels and its applications have been conducted over centuries by scientists, and in this section a brief description of gels will be introduced.

2.1.1 Definition of a gel

Commonly a gel, in its steady solid state, is a soft material that possesses three dimensional cross-linked networks. By using different characterization methods, gels are defined in different ways. The elasticity of gels is reflected by its rheological definition. In area of rheology, the storage modulus $G'$, and loss modulus $G''$ of a gel, are independent of frequency, and the $G'$ is much larger than $G''$ since in gels elasticity plays a leading role when compared with viscosity\(^6\), \(^7\). Flory has defined gel as a material in which liquid is trapped inside the three dimensional networks generated by a gelator due to the surface tension and capillary forces\(^7\), \(^8\).

2.1.2 Categories of gels

Gels could be mainly divided into three categories as hydrogels, organogels and xerogels. Either via chemically crosslinking or physically crosslinking a gelator forms
a three dimensional network and thus the liquid is imprisoned inside the network and then a gel is produced. The physically crosslinked network of a gel is usually formed by polymer chains or small molecule chains held together through non-covalent interactions. Among various numbers of gelators, low molecular mass organogelators (LMOGs) are quite important due to its significant gelation ability. Low molecular mass organogelators usually possess a molecular mass as low as 2000Da, with a low concentration of the LMOGs, mass amount of solvent would be trapped in the network the gelator generates by effects such as self-assembly.

2.1.3 Applications of gels

Gel productions such as make ups and skin care goods, tissue replacements for human organs could be used on the human body. Gels also have been widely used in the area of medical industry, for some drugs that need to be stored under certain conditions, gels can be used to produce the pack which can help to keep the drugs from losing the their efficacy and can be applied during the drug delivery. Food or raw materials produced using gels such as gelatin have now been one of the essential goods in common life.
2.2 Introduction to double-network gels

Over recent years, scientists have shown an interest in the study of gels which consists of two components that are physically bonded with each other or individually dispersed in the solvent. The first kind of this gel was reported in 1993 by Hanabusa and his co-workers\textsuperscript{15}, they reported a “two component” gel in which barbituric acid and pyrimidine units are bonded through hydrogen bonds, the scheme is shown in figure 2-1.

![Figure 2-1 Barbituric acid and pyrimidine units bonded with each other in solvent](image)

Figure 2-1 Barbituric acid and pyrimidine units bonded with each other in solvent thus generates a two component network to form a gel.

The two components in figure 2-1 are attracted to each other through hydrogen bonds to form a complex network, thus a huge, complex network is obtained. Following the achievements of Hanabusa, scientists including Mülhaupt\textsuperscript{48} and Shinkai\textsuperscript{49} made use of that idea and accomplished some further investigations by
using different types of the two compounds or changing the weight percent of the two compounds, thus the “two component” gel was further developed\textsuperscript{16}.

Afterwards, more investigations were carried out. Professor J. P. Gong and her co-worker found a “double network” hydrogel\textsuperscript{17} which is produced by combining gelatin with bacterial cellulose, it is pointed out that this combination of a stiff, brittle network and a soft, ductile second network is completely different from those traditional polymer networks\textsuperscript{17}. It is also pointed out that the ratio of the two gelators has a very important influence on the properties of the gel\textsuperscript{17}. This distinguishing gel has a mechanical strength as high as several megapascals despite containing 90\% water, which gives it the potential to be used as tissue replacements such as artificial articular cartilage\textsuperscript{17}.

Richard Spontak with his research colleagues carried out some experiments to investigate a two-network system where 1, 3:2, 4-dibenzylidene-D-sorbitol (DBS) gelator is combined with a series of midblock swollen triblock polymer gelators differing in molecular weight\textsuperscript{18}. DBS is among those low mass molecule gelators (LMOG), which possesses the ability to form self-assembled fibrillar networks (SAFINs), and those polymer gelators would prefer forming self-assembled micellar networks (SAMINs). Both of the networks are generated via physical effects. It is confirmed by data acquired in experiments that the mechanical properties like the network integrity is strongly dependent on whether the SAMIN or the SAFIN forms first during the cooling step of the gelation\textsuperscript{18}. The two networks would have support to each other if the SAMIN forms at a much lower temperature than SAFIN and the
two networks have a minor effect on each other’s thermo properties. However in the reversing order of network forming, the SAMIN damages the SAFIN since the SAFIN is relatively fragile, a complete SAFIN cannot be formed as not all DBS could participate in forming an integral network. But those remaining DBS molecule would interact with micelles in the SAMIN via physical effects and as a result of that the SAMIN is stabilized and thermal properties of SAMIN are enhanced\textsuperscript{18}.

2.3 Maximum bubble pressure method

The maximum bubble pressure method was invented over a century ago and has been studied by scientists. In this section, the summarized introduction and research background of maximum bubble pressure method will be introduced.

2.3.1 Introduction of maximum bubble pressure method

In 1851, Simon proposed the maximum bubble pressure (MBP) tensiometry to be used in measuring the surface tension of liquids with surfactants\textsuperscript{46}. The experiment method refers to a testing method where a bubble is generated in a fluid or gel by pressurized air in an open capillary. Bubble growth is resisted by the surface tension and viscosity of sample being probed. The maximum bubble pressure occurs when a semi-spherical cap is generated at the capillary opening. After which it grows rapidly resulting in a pressure drop. A scheme showing the variation of shape of bubble and pressure inside the bubble is shown in figure 2-2.
Nevertheless, this method was not widely adapted by scientists\textsuperscript{19} because it was believed that there were several factors that might have caused the imprecise of the measurement results, such as the viscosity of the sample. But many significant contributions were made to improve and develop this technique.\textsuperscript{19,20} Professor V.B. Fainerman\textsuperscript{21} pointed out in one of his research that the Laplace equation can be corrected and expressed as:

$$\gamma = f \frac{r(P_s - P_h)}{2} - \Delta \gamma_a - \Delta \gamma_v$$

(Equation 1.1)

where $\gamma$ represents the surface tension, $f$ is the correction factor, and $r$ is the bubble radius when the bubble becomes semi-spherical (same as the inner radius of capillary), $P_s$ is the pressure in the measuring system, $P_h$ is the hydrostatic
pressure of the liquid at the capillary tip, $\Delta \gamma_a$ is the surface tension caused by aerodynamic resistance and $\Delta \gamma_v$ is the surface tension caused by viscous hydrodynamic resistance of the liquid.\textsuperscript{22-26} Maximum bubble pressure method has been proved as a very useful method that widely used in measuring surface tension in many fields including industrial and biological applications.\textsuperscript{27-33}

2.3.2 Maximum bubble pressure rheology in characterization of gel properties

Recently, maximum bubble pressure rheology was developed to be used to characterization the properties of soft materials such as polymer hydrogels by Crosby and his co-workers.\textsuperscript{5} Figure 2-3 shows an illustration of devices used to carry out the maximum bubble pressure measurements.

![Illustration of devices used in the maximum bubble pressure measurements.](image)

Figure 2-3 Illustration of devices used in the maximum bubble pressure measurements.
The combination of devices consists of a gastight syringe pump, a stainless syringe with needles, a pressure sensor, a strain meter, a digital converter and a computer. Before the test, the syringe needle is lowered into the soft material, and then the air is pumped into the syringe then to the tip of the needle at a constant rate using the syringe pump. The pressure of the system is sensed by the pressure sensor and data acquired is delivered to the computer. The pressurization inside the soft material will either result in an elastic reversible cavitation, which was caused by reversible deformation of the network, or an irreversible fracture. Both cavitation and fracture occurs at a maximum pressure. The obtained maximum bubble pressure can be used to calculate the modulus of the sample with equation 1.2 and 1.3 in case of cavitation or fracture respectively.

\[ P_c = \frac{2\gamma}{r} + \frac{5}{6}E \]  
(Equation 1.2)

\[ P_f = \left(\frac{\pi EG_c}{3}\right)^{1/2} \left(\frac{1}{r}\right)^{1/2} \]  
(Equation 1.3)

where \( P_c \) is the critical pressure caused by cavitation, \( \gamma \) is surface tension, \( r \) is inner needle radius, \( E \) is modulus, \( P_f \) is the critical pressure caused by fracture and \( G_c \) is strain energy release rate.\(^{34}\)

As suggested by Crosby,\(^{35}\) compared to other methods, maximum bubble pressure method has two unique advantages when measuring gel modulus: it can measure the modulus of the soft material including a part of a living being; and it would be possible to measure the modulus of the material at an arbitrary point within the material at a very small length scale, from 0.1 to 1000μm due to different needle
sizes, using a rather small needle could gain much accurate results of maximum pressure. This technique has been applied to characterize a number of soft materials, such as biological tissues\textsuperscript{12, 11, 36} and self-assembled polymer solutions\textsuperscript{37, 38, 34, 39}.

2.4 Introduction to gelators and the solvents

All types of gelators used in this research and their gelation mechanisms will be introduced in this section.

2.4.1 Dibenzylidene sorbitol and dimethyldibenzylidene sorbitol gelator

![Chemical structure of dibenzylidene sorbitol](image)

Figure 2-4 Chemical structure of dibenzylidene sorbitol
Dibenzylidene sorbitol and its derivatives are good gelling agents to various solvent among those LMOGs. The existence of both hydrophobic phenyl rings and polar hydroxyl groups allows it to dissolve in a large quantity of solvents. Hydrogen bonds formed between molecules construct networks, and thus results to the gelation of solvents.

2.4.2 12-hydroxystearic acid gelator

12-HSA is a structurally simple, commercially available small molecule organogelator. Investigations have been done to discuss gel properties using the 12-HSA as a LMOG (gelator). It is applied in areas like food science, organic electronics and gas separation.\textsuperscript{40, 41} During the cooling step from liquid state to solid state, the 12-HSA molecules crystallize by forming head-to-head dimers and thus a network is generated to trap fluid inside\textsuperscript{42}. The chemical structure of 12-hydroxystearic acid is shown in figure 2-6 and a schematic diagram of stereochemistry of 12-hydroxystearic is shown in figure 2-7.
2.4.3 Poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) gelator

Figure 2- 6 Chemical structure of 12-hydroxystearic acid.

Figure 2- 7 Schematic diagram of stereochemistry of 12-hydroxystearic acid.

Figure 2- 8 Chemical structure of Poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer.

Figure 2-8 displays the chemical structure of the SEBS block copolymer, the PS block, the so called hard block, is stiff due to the presence of benzene, while the PEB block, the soft block, is quite soft and flexible. The hard block functions as the conjunction point of the soft chains, with numbers of structures like this the three dimensional network is generated.
2.4.4 Network dispersed in double-network gel

Figure 2-9 Poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer and 12-hydroxystearic acid dispersed in mineral oil.

Figure 2-9 shows the way two networks are dispersed together in one gel system. The addition of 12-HSA networks increases the network density in the whole system. Changes over physical properties within the two-network gel will be investigated through experiments and results will be discussed in the thesis.
CHAPTER Ⅲ

EXPERIMENTAL METHODS

3.1 Materials

All materials used in the research and the purification method will be described in the following section.

3.1.1 Chemicals used as received

Dibenzylidene Sorbitol (Milliken Chemical), Dimethyldibenzylidene sorbitol (Milliken Chemical), Polyethylene glycol 400 (Alfa Aesar), o-xylene, p-xylene, Poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer (Kraton, G1650 MU-N-P-), Toluene, mineral oil (PFEIFFER, D-35614), ethyl acetate, hexane (Fisher Scientific Co., 99.9%).

3.1.2 Chemicals used after purification

12-hydroxystearic acid (12-HSA, Tokyo Kasei Kogyo Co., Ltd., >75.0%) was purified by a method that was previously reported. 12-HSA (received from manufacturer) was dissolved in a mixture of ethyl acetate: hexane (1:19 v: v) at 70 °C. The solution was then cooled very slowly while stirring vigorously to allow the 12-HSA to precipitate without forming a gel. Purified 12-hydroxystearic acid was kept under room temperature.
3.2 Preparation of gels

The DBS-PEG and DMDBS-PEG gel samples were prepared by dissolving gelators in PEG 400 on a hot plate with constant agitation and under nitrogen environment. Temperatures needed were 130°C and 170°C respectively. After the solid gelator was completely dissolved and the mixture became transparent, the solution was removed from the hot plate. The mixture was separated into 20ml vials and was allowed to cool down to room temperature. Gel sample in vials were stored for 2 hours before use. The mass fractions of DBS-PEG and DMDBS-PEG gels were 3% and 1% respectively.

The mineral oil was combined together with 12-HSA and SEBS in a round-bottom flask, a small amount of toluene as the co-solvent was added into the flask and the mixture was stirred under 120 °C until it turned into a transparent, homogeneous fluid, then a rather viscous liquid was obtained through being rotational evaporated. Then, the production is dispersed into 20ml vials and the vials were put in the vacuum oven under 120°C for 12 hours to remove the toluene remnant. Gel samples were cooled under room temperature until the gel forms. Gel samples in the vials were used in the following experiments.
Three tables above show compounds of different concentrations used to prepare the gel samples. One vial of pure mineral oil and one vial of pure PEG 400 were also used in the maximum bubble pressure tests.

3.3 Preparation of samples for rheological tests

Disk like samples for rheological tests which possess a measurement of 1.9mm height and 2.5mm diameter were prepared by compression molding. The upper and
lower plates as well as the mold used were preheated and the sample was put in the mold and the mold was placed into two hot plates, with an applied constant force from the upper plate. The upper and the lower plate were released for several times to allow air to escape. The procedure above was repeated for 3 times for each preparation. The temperature and pressure was kept at 120°C and 5000psi respectively during the compressing procedure to get uniform disk samples without bubbles inside. The figure listed below is a scheme showing the process of sample preparation.

![Process of preparing disk like samples for rheological tests.](image)

3.4 Characterization methods

All characterization methods used in this research and the related parameters will be introduced in this section.
3.4.1 Tilting tests

Tilting tests are the most common test of gelation by tilting a testing tube or vial containing the gel sample 90° or 180°. In this research, the vials containing gel samples were tilted 90° after heating to the desired temperatures and were equilibrated for 10 min before each test. Pictures took during the measurements were put together to be analyzed and to determine the gel transition temperature.
3.4.2 Maximum bubble pressure rheology measurements

Maximum bubble pressure rheology measurements were carried out with an apparatus described in the table below.

Table 3-4 Components of maximum bubble pressure apparatus

<table>
<thead>
<tr>
<th>Device</th>
<th>Model</th>
<th>Parameters Related</th>
</tr>
</thead>
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<td>Volume Of 19.13ml</td>
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<td>Hamilton stainless steel</td>
<td>18 gauge</td>
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<td>Px26 Series.</td>
<td>30 Psi</td>
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<td>Model DI-145</td>
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<tr>
<td>White Wiring Connector</td>
<td>CX136-4 Push-On</td>
<td></td>
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<td></td>
<td>Connector(Omega)</td>
<td></td>
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</tbody>
</table>

Software called Windaq matching the digital converter was used in the measurement. All data collected using the Windaq software were converted into excel or origin files.
3.4.3 Rheological tests for SEBS/M.O. gel and the double-network gel

A DHR-2 rheometer with the parallel plates (25mm diameter) was used to characterize the rheological properties of gel samples in the oscillatory mode.

Oscillatory strain sweeps were performed to determine the linear viscoelastic region and the critical strain at 50°C and 80°C, respectively. The strain sweep was conducted at a frequency of 100 rad/s over a strain range of 0.01% to 100%.

Dynamic temperature sweeps were conducted over the temperature range from 30°C to 120°C at a heating rate of 5°C /min at a frequency of 1 rad/s, with strain amplitudes of 1.25%.

Oscillatory frequency sweeps were conducted over the frequency range of 0.01 rad/s to 100 rad/s. The tests were carried out from the temperature of 35°C to 95°C, with an increment of 10°C. The strain amplitude was set as 1% below 80°C, and 10% from or over 80°C for 12-HSA+SEBS/M.O. gel and 1% below 80°C and 4% from or over 80°C for SEBS/M.O. gel in the experiments.
CHAPTER IV
RESULTS AND DISCUSSIONS

4.1 Gel transition temperature measured by tilting tests and maximum bubble pressure method

The gel transition temperatures of DBS/PEG 400 gel and DMDBS/PEG 400 gel were measured by both the tilting tests and the maximum bubble pressure tests.

4.1.1 Characterization of DBS/PEG 400 gel transition temperature

The following section introduces the gel transition temperatures measured by the tilting test and the maximum bubble pressure method.

4.1.1.1 DBS/PEG 400 gel transition temperature characterized by tilting test

![Image showing DBS gels tilted at different temperatures](image)

Figure 4-1 DBS gels tilted to 90 degree angle during tilting tests
Figure 4-1 displays imagines of the tilted vials with DBS/PEG 400 gels during tilting tests. Below 75°C, the gel system was a solid gel and able to keep the initial physical shape when the vial was tilted 90°. At 80°C, the three dimensional network started to collapse and the system was too weak to hold the initial shape. Above 85°C, the gel system became a homogeneous solution and flows randomly in the vial, and no solid gel was observed. The gel transition temperature, $T_{\text{gel}}$, was determined at which the gel system begins to fracture, and then the $T_{\text{gel}}$ of DBS/PEG 400 gel was characterized as 80°C by the tilting test method.

4.1.1.2 DBS/PEG 400 gel transition temperature characterized by maximum bubble pressure method

![Figure 4-2 Maximum pressure plotted as a function of temperature.](image-url)
Figure 4-2 shows plots of maximum bubble pressure versus temperature. Maximum bubble pressure of the 3% DBS/PEG 400 gel was measured from 60°C to 95°C with an increment of 5°C between each test. The maximum pressure remains almost the same value at the temperature of 60°C and 65°C, while from 65°C, the maximum pressure decreases fast as the temperature continues to increase. At the temperature of 85°C, the maximum pressure drops to the lowest value and remains almost the same value and is independent of temperature from that on, indicating the gel has completely turned into liquid state. Thus the solid to liquid state gel transition temperature of 3% DBS/PEG 400 gel can be noted as 85°C.

4.1.2 Characterization of DMDBS/PEG 400 gel transition temperature

The following section introduces the gel transition temperatures measured by the tilting test and the maximum bubble pressure method.
4.1.2.1 DMDBS/PEG 400 gel transition temperature characterized by tilting test

Figure 4-3 displays images of the tilted vials with DMDBS/PEG 400 gels during tilting tests. Below 90°C, the gel system was a solid gel and able to keep the initial physical shape when the vial was tilted 90°. At 95°C, it was observed that the surface of the gel started to incline due to gravity and the gel system could not hold its initial shape any more. At 100°C and 105°C, larger shape transforms were observed and the gel was weaker. However, a total break of the gel shape didn’t occur under these temperatures. At 110°C, the three dimensional network started to collapse and the system was too weak to hold the initial shape. Above 115°C, the gel system became a homogeneous solution and flows randomly in the vial, and no solid gel was observed. As discussed above, the T_{gel} of DMDBS/PEG 400 gel was determined as 110°C by the tilting test method.
4.1.2.2 DMDBS/PEG 400 gel transition temperature characterized by maximum bubble pressure method

Figure 4-4 Maximum pressure plotted as a function of temperature.

Figure 4-4 shows plots of maximum bubble pressure versus temperature. Maximum bubble pressure of the 1% DMDBS/PEG 400 gel was measured from 65°C to 120°C with an increment of 5°C between each test. The maximum pressure changes little from the temperature of 65°C to 100°C, while from 105°C, the maximum pressure decreases significantly as the temperature continues to increase. At the temperature of 115°C, the maximum pressure drops to the lowest value and remains almost the same value and is independent of temperature from that on, indicating the gel has completely turned into liquid state. Thus the solid to liquid state gel transition temperature of 1% DMDBS/PEG 400 gel can be noted as 115°C.
The gel transition temperatures measured by tilting tests and maximum bubble pressure method were list in table 4-1, and results from maximum bubble pressure were both 5°C higher than those from tilting tests.

It is believed and confirmed during the experiments that gel could be very fragile at temperatures close enough to its transition temperature, and the three dimensional network could be easily destructed thus fracture might occur if the gel sample in the vial was not tilted gently, even when the temperature was still below $T_{gel}$, then the gel transition temperature measured by tilting tests could be underestimated, and the arbitrariness could be a disadvantage of the tilting test method and in turn is an advantage of the maximum bubble pressure method as the gel sample was kept stable during the whole measurement. However, the tilting test still gives the proper scaling that can be used in other similar characterizations.

### 4.2 Study of the double-network gel

The following section introduces the study of the double-network gel by both maximum bubble pressure method and oscillatory shear rheology.

<table>
<thead>
<tr>
<th></th>
<th>Tilting</th>
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<tbody>
<tr>
<td>DBS-PEG 400</td>
<td>80°C</td>
<td>85°C</td>
</tr>
<tr>
<td>DMDBS-PEG 400</td>
<td>110°C</td>
<td>115°C</td>
</tr>
</tbody>
</table>
4.2.1 Preparation of gels

Figure 4-5 Appearance of SEBS/M.O. gel samples with different concentrations.

Figure 4-6 Appearance of 12-HSA+SEBS/M.O. gel samples with different concentrations.
The two figures of 4-5 and 4-6 shows the appearance of gel samples prepared. The 5%, 10% and 15% gel samples were transparent, colorless and possesses smooth upper surfaces, indicating that the gel samples were well prepared and that additional forces applied during the producing process were removed during the heating-cooling step, thus the systems were in homogeneous state. However, due to the high weight percent of SEBS component, the other three gel samples would not turn into liquid state unless a high temperature environment was provided. These three gel samples were then heated in a hot plate under 130°C for 4hrs, a slight color change was observed in the three two-network gel samples. The gel samples appeared to be a little bit yellow, which might be caused by the degradation of 12-HSA component, and the bubbles in the gel would not disappear, which means that the three two-network gel samples still need higher temperature to turn into a viscous liquid state. As a result of that, 130°C could be the upper limit in temperature under which the 12-HSA+SEBS/M.O. gels can be produced. Gels chosen to be used in the following experiments were: 1)5% SEBS/M.O., 2)1% 12-HSA+5% SEBS/M.O., 3)10% SEBS/M.O., 4)1% 12-HSA+10%SEBS/M.O., 5)15% SEBS/M.O., 6)1% 12-HSA+15% SEBS/M.O., 7)1% 12-HSA/M.O.

4.2.2 Maximum bubble pressure measurements

The maximum bubble pressure was measured by the device set up as discussed in the previous chapter. Gel samples were heated every 10°C from 25°C to 115°C. The
gels were equilibrated for 10 min before each test. At each temperature, three measurements were conducted and the average value and deviation were calculated. The error bar is indicated in every figure.

4.2.2.1 Maximum bubble pressure measurement on 12-HSA/M.O. gel

![Graph of maximum bubble pressure versus temperature for 1% 12-HSA/M.O. gel.](image)

Figure 4-7 Plots of maximum bubble pressure versus temperature for 1% 12-HSA/M.O. gel.

The figure listed above shows plots of maximum bubble pressure versus temperature. Maximum bubble pressure of the 1% 12-HSA gel was measured from 25°C to 115°C with an increment of 10°C between each test. The maximum pressure drops slowly from the temperature of 25°C to 35°C, while from 35°C, it decreases fast as the temperature continues to increase. At the temperature of 75°C, the maximum
pressure drops to the lowest value and is almost independent of temperature from that on, indicating the gel has completely turned into liquid state. Thus the solid to liquid state gel transition temperature of 1% 12-HSA/M.O. gel can be noted as 75°C.

4.2.2.2 Maximum bubble pressure measurement on SEBS/M.O. gel

![Figure 4-8 Plots of maximum bubble pressure versus temperature for 5%, 10% and 15% SEBS/M.O. gel.](image)

Each of the three plots in figure 4-4 shows a similar trend as the plot in temperature sweep for 12-HSA/M.O. gel. The maximum bubble pressure drops in a slow-fast-slow velocity mode as the temperature increases, and as the temperature reaches 75°C, the maximum bubble pressure of 5% SEBS/M.O. drops to its lowest value and is independent of the increase of temperature. For the 10% and 15%
SEBS/M.O. the maximum bubble pressure drops to the minimum level at 85°C and 105°C respectively. The maximum bubble pressure which is directly related to the local modulus is increased as the weight percent of SEBS component is increased. A quite larger increment in the maximum bubble pressure from 10% to 15% is observed when compared with the increment from 5% to 10%, which is attributed to the increase of network density. The gel transition temperatures for 5%, 10% and 15% SEBS/M.O. gels were 75°C, 85°C and 105°C.

4.2.2.3 Maximum bubble pressure measurement on the double-network gels.

Figure 4- 9 Plots of maximum bubble pressure versus temperature for 5%, 10% and 15% double-network gels.
The maximum bubble pressures for the three types of double-network gels are plotted as a function of temperature in figure 4-9. One more measurement under 30°C is conducted for each of the blends tested in order to study more clearly the maximum bubble pressure change under low temperatures. The critical pressure drops slowly below 35°C, and a significant decrease from 35°C to 45°C occurs and a shoulder is observed, before which the maximum bubble pressure drops slowly while after which the maximum bubble pressure decreases sharply until 45°C. As is shown in figure 4-7, the maximum bubble pressure of 1% 12-HSA/M.O. gel begins to drop at 35°C, indicating that the 12-HSA component provides less and less elasticity to the double-network gel system, resulting into a significant drop in the plots of figure 4-9. From 60°C, the maximum pressure drops as the temperature increases. As the temperature rises to 75°C, $T_{gel}$ of the 1% 12-HSA/M.O. gel, the maximum bubble pressure of the two-network system drops to a quite close value as that of the SEBS/M.O. gel. And finally it reaches the minimum value and remains the same as the temperature continues to increase, which means the double-network system has turned into liquid state. The gel transition temperatures for 5%, 10% and 15% two-network gels were noted as 75°C, 85°C and 105°C.
Figure 4- 10 Plots of $P_{\text{MAX}}$ (double-network gel), $P_{\text{MAX}}$ (12-HSA) $+P_{\text{MAX}}$ (SEBS) versus temperature for 5%, 10% and 15% gels.
Figure 4-11 Plots of \( P_{\text{MAX}} \) (blend)/ \((P_{\text{MAX}} \ (12-\text{HSA}) + P_{\text{MAX}} \ (\text{SEBS})) \) versus temperature for 5%, 10% and 15% gels.

\( P_{\text{MAX}} \) (blend) and \( P_{\text{MAX}} \ (12-\text{HSA}) + P_{\text{MAX}} \ (\text{SEBS}) \) were plotted as a function of temperature in one figure. By making a comparison, the extent to which the maximum bubble pressure of the double-network system is promoted could be analyzed. Each of the three plots in figure 4-11 shows a descending trend over the temperature range of 25°C to 115°C, which means that the effect 12-HSA brings to the two-network system weakens at high temperature.

The enhancement in maximum bubble pressure of SEBS/mineral oil gels by 12-HSA component was observed in the maximum bubble pressure measurements. Further quantitative study is carried out with oscillatory shear measurements.
4.2.3 Rheological tests

The 10% SEBS/M.O. and the 10% blend were chosen to be used in the rheological test to further investigate the rheological behaviors of the two-network gel system. Test samples were produced as procedures introduced previously.

4.2.3.1 Rheological tests for 10% SEBS/M.O. gel

Two oscillation strain sweep were conducted at 50°C and 80°C with a frequency of 100 rad/s over a strain range of 0.01% to 100%.

![Graph](image)

Figure 4- 12 Plots of storage modulus $G'$ and loss modulus $G''$ versus strain amplitude for 10% SEBS/M.O. gel at two temperatures. $G'$, 50°C (■), 80°C (▲); $G''$, 50°C (●), 80°C (▼).
Figure 4-12 shows the strain sweeps of the 10% SEBS/M.O. gel. Both the storage and loss modulus $G'$ and $G''$ are independent of the strain when the strain is below 1% and 4% respectively under two temperatures, and $G'>G''$, thus the material is intact and possesses a solid-like behavior. At 50°C and 1% strain, the storage modulus begins to decrease sharply and intensively, the increasing strain disrupts network structure, the system behaves more fluid-likely. At the same strain and temperature (50°C and 1% strain), a significant increase of $G''$ is observed in the plot, which could be also caused by the increasing strain doing more damage to the intact structure of the material. Under both temperatures, the loss modulus standing for viscosity becomes slightly larger than the storage modulus which represents the elasticity at and after the critical strain. The critical strain is obtained as 1% at 50°C. At 80°C, the storage modulus begins to fall at 4% strain, and same changes of $G''$ as that of the 50°C sweep is observed. The critical strain under this circumstance is obtained as 4%.

A temperature sweep was conducted over a temperature range of 30°C to 120°C, with an increasing step of 5°C/min, and the strain amplitude and the frequency were set as 1.25% and 1rad/s respectively.
For the 10\% SEBS/M.O. Gel, figure 4-13 shows the plots of storage modulus $G'$ and the loss modulus $G''$ versus temperature. Figure 4-14 shows the plots of $\tan(\delta)$ versus temperature.
versus temperature. The storage modulus standing for elasticity of the system decreases as the temperature increases, which means the elastic property is weakened as the temperature goes higher, while the loss modulus increases and reached a peak, and then decreases though still has a larger value than the storage modulus, which means the energy lost due to viscous flow increases as the temperature rises, but when it comes to be in a pretty high temperature environment, viscosity of the system decreases as well as the elasticity. The transition temperature of the SEBS/M.O. gel is observed at 85°C, where the storage modulus starts to drop dramatically and plots of G’ and G” intersects. Beyond point of the transition temperature, G’ is larger than G”’, indicating that the elastic behavior predominates the viscous behavior, while after 85°C, G” overcomes G’ and the system is dominated by the viscous behavior. Tan (delta) also begins to rise sharply at the temperature of 85°C. The result is consistent with data acquired from the maximum bubble pressure measurements.

An oscillatory frequency sweep was conducted over the frequency range of 0.01rad/s to 100rad/s. The tests were carried out from the temperature of 35°C to 115°C, with an increment of 10°C. The strain amplitude was set as 1% below 80°C, and 4% at 80°C and above in the experiments.
Figure 4-15 Plots of oscillation torque versus frequency for 10% SEBS/M.O. gel at seven temperatures. The dash-dot line indicates the minimum torque limit of the machine.

As pointed out in figure 4-15 by the dash-dot line, the minimum torque within the rheometer’s measuring range is 2μN.m, and there are 5 points below the dash-dot line in 95°C plot, these unreasonable data were deleted in figure 4-16 to 4-18.
Figure 4-16 Plots of storage modulus $G'$ versus frequency for 10% SEBS/M.O. gel at seven temperatures.

Figure 4-17 Plots of loss modulus $G''$ versus frequency for 10% SEBS/M.O. gel at seven temperatures.
Figure 4-16 and 4-17 display plots of $G'$ and $G''$ versus frequency under different temperatures. At low temperatures, $G'$ shows a slight change in response to the variation of frequency, and it increases a little bit as the frequency increases, a shorter relaxation time is obtained due to a higher frequency, indicating that the gel is quite rigid under this temperature. At low temperatures, the loss modulus also shows an independence of the frequency increase. However, at higher temperatures, the storage modulus increases a lot as the frequency increases. Both $G'$ and $G''$ are almost independent on frequency $\omega$ when the measuring temperature is under $85^\circ$C, and the slope of the $G'$ plot is much less than 2 and the slope of the $G''$ plot is much less than 1. Under $85^\circ$C, the slope of $G'$ versus $\omega$ becomes 2 and the slope of $G''$ versus $\omega$ becomes 1 in the terminal region. According to Han$^{45}$ and Doi-Edwards theory$^{50}$, when in thermodynamically disordered liquid state, $G'$ and $G''$ could be expressed as:

$$G' = \frac{8}{\pi^2} G_0 \sum_{p, \text{odd}} \frac{1}{p^2} \left( \frac{\omega \lambda_p}{1 + (\omega \lambda_p)^2} \right)^2$$

(4.1)

$$G'' = \frac{8}{\pi^2} G_0 \sum_{p, \text{odd}} \frac{1}{p^2} \left( \frac{\omega \lambda_p}{1 + (\omega \lambda_p)^2} \right)$$

(4.2)

In the equations above, $\lambda_p = \tau_p / p^2 (p=1, 3, 5 \ldots)$ in which $\tau_p = L^2 / D \pi^2$ is the disengagement time, where $L$ is a contour length, $D$ is the curvilinear diffusion constant and $G_0$ is a constant. For $\omega < \frac{1}{\lambda_p}$ (terminal region), $1 + (\omega \lambda_p)^2 \approx 1$ and then $G' \propto \omega^2$, $G'' \propto \omega$. Thus the transition temperature obtained for the 10% SEBS/M.O. gel is $85^\circ$C.
Figure 4-18 Plots of tan (delta) versus frequency for 10% SEBS/M.O. gel at seven temperatures.

According to Winter and Mours\textsuperscript{44}, under the transition temperature the loss tan (delta) should be independent of the frequency. Nevertheless, data plot shown in figure 4-18 does not fit this theory, and this might be caused by the remaining viscoelasticity in the gel caused by the gelator.
4.2.3.2 Rheological tests for the 10% blend

Two oscillation strain sweeps were measured at 50°C and 80°C with a frequency of 100 rad/s over a strain range of 0.01% to 100%.

Figure 4-19 Plots of storage modulus G’ and loss modulus G’’ versus strain amplitude for the 10% blend at two temperatures. G’, 50°C (■), 80°C (▲), G’’, 50°C (●), 80°C (▼).

Figure 4-19 shows the strain sweeps of the two-network system. The disorder of points at low strains could be caused by the error of the test caused by the limitations of the machine. Both the storage and loss modulus G’ and G’’ are independent of the strain when the strain is below 1% and 10% respectively under two temperatures. At 50°C and 1% strain, the storage modulus begins to slowly decrease, unlike the sudden drop happened to the one-network system, and the 12-HSA network addition enables
the two-network gel system to transit smoothly with a rather slow elasticity loss rate, making the transition process more gentle. The critical strain is obtained as 1% for 50°C. At 80°C, the storage modulus begins to fall at 10% strain; the critical strain is obtained as 10%.

As a result of the strain sweep, the following frequency sweep would be carried out at the strain of 1% when the temperature is below 80°C and at the strain of 10% when the temperature comes above 80°C.

A temperature sweep were conducted over a temperature range of 30°C to 120°C, with an increasing step of 5°C/min, and the strain amplitude and the frequency were set as 1.25% and 1 rad/s respectively.

Figure 4-20 Plots of storage modulus $G'$ and loss modulus $G''$ versus temperature for the 10% blend.
Figure 4-21  Plots of tan (delta) versus temperature for the 10% blend.

For the double-network gel system, figure 4-20 shows the plots of storage modulus $G'$ and the loss modulus $G''$ versus temperature. Figure 4-21 shows the plots of tan (delta) versus temperature. The storage modulus begins to descend at the temperature of $35^\circ C$, and a small shoulder is observed at $35^\circ C$, from where the 12-HSA network is weakened thus provides less and less elasticity to the gel system, resulting in a drop of the storage modulus. The gel to solution transition process of 12-HSA network occurs at a much lower temperature than that observed in figure 4-7, this could be attributed to the fact that SEBS network forms in an earlier sequence than the 12-HSA network during cooling, part of 12-HSA molecules could not take part in forming networks, the overall 12-HSA density is lowered. As the temperature rises up to $60^\circ C$ and keeps increasing, the storage modulus of the two-network gel begins falling sharply and finally comes to a close value of the loss modulus. The loss
modulus $G''$ increases as the temperature goes higher from 30°C, and then begins to decrease at 65°C and finally overcomes the storage modulus at a rather high temperature. The transition temperature of the two-network system is observed at 85°C, which is consistent with results measured by the maximum bubble pressure experiment.

$G'$ of the double-network gel is a little bit larger than double the value of $G'$ of the single-network gel at low temperatures when comparing the two figures 4-13 and 4-20, which is also consistent with the result obtained from the maximum bubble pressure test. However, at a higher temperature, the enhancement in elastic modulus is decreased. The elastic modulus of the two-network system is significantly increased with the addition of 12-HSA network at low temperatures.

An oscillatory frequency sweep was conducted over the frequency range of 0.01rad/s to 100rad/s. The tests were carried out from the temperature of 35°C to 115°C, with an increment of 10°C. The strain amplitude was set as 1% below 80°C, and 10% at 80°C and above in the experiments.
Figure 4-22 Plots of oscillation torque versus frequency for the 10% blend at seven temperatures. The dash-dot line indicates the minimum torque limit of the machine.

As is pointed out in figure 4-10, the minimum torque within the rheometer’s measuring range is 2μN.m, and there are 2 points below the dash-dot line in 95°C plot, these unreasonable points were also deleted in the figure 4-23 to 4-25.
Figure 4-23 Plots of storage modulus $G'$ versus frequency for the 10% blend at seven temperatures.

Figure 4-24 Plots of loss modulus $G''$ versus frequency for the 10% blend at seven temperatures.
Figure 4-23 and 4-24 display plots of $G'$ and $G''$ versus frequency under different temperatures. Both $G'$ and $G''$ are almost independent on frequency $\omega$ when the measuring temperature is under 85°C, and the slope of the $G'$ plot is much less than 2 and the slope of the $G''$ plot is much less than 1. Under 85°C, the slope of $G'$ versus $\omega$ becomes 2 and the slope of $G''$ versus $\omega$ becomes 1 in the terminal region. As discussed above, the gel transition temperature obtained for the 10% blend is 85°C.

![Plot of tan(\delta) versus frequency for the 10% blend at nine temperatures.](image)

Figure 4-25 Plots of tan(\delta) versus frequency for the 10% blend at nine temperatures.

Tan (delta) in figure 4-25 does not fit the theory proposed by Winter and Mours\textsuperscript{44} either, and this similarly could be caused by the effect of gelators.
CHAPTER V

CONCLUSION

The transition temperature of DBS/PEG 400 and DMDBS/PEG 400 gels were characterized by tilting tests and maximum bubble pressure method, results obtained from tilting tests were both 5°C lower than that from the maximum bubble pressure measurements, the arbitrariness of tilting test highlighted the accuracy of the maximum bubble pressure method, which remains the testing sample in a stable process during the experiment and gives people a more quantified observation of the measurement.

The elastic modulus of the SEBS+12-HSA/M.O. double-network gel is greatly enhanced under low temperatures where the gel possesses solid-like behaviors by adding a micro quantity of 12-HSA when compared with the SEBS/M.O. single-network gel. The transition temperature of SEBS/M.O. gel is not affected by the 12-HSA component, but the solid-fluid transition process is more smooth due to the existence of low mass molecule organogelator 12-HSA.

Further investigations of this double-network gel system would be interesting. Future work such as studying the relationship between the increment of double-network’s modulus at low temperatures and the additive quantity of 12-HSA, or other compounds capable of forming a double-network gel could be carried out to study the physical properties of the double-network gel system.
REFERENCES


54


