Self-healing Supramolecular nanocomposites

Zhen Liu
Self-healing Supramolecular nanocomposites

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof.ir. K.C.A.M. Luyben,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op 23 February 2015 om 15.00 uur

door

Zhen Liu

Master of Science in Biochemical Engineering, Delft University of Technology
geboren te Harbin, China.
Dit proefschrift is goedgekeurd door de promotoren:

Prof. Dr. S.J. Picken

Copromotor: Dr. Ir. N.A.M. Besseling

Samenstelling promotiecommissie:

Rector Magnificus voorzitter
Prof. dr. S.J. Picken Technische Universiteit Delft, promotor
Dr. ir. N.A.M. Besseling Technische Universiteit Delft, copromotor
Prof. dr. ir. J. van der Gucht Wageningen Universiteit
Prof. dr. E.J.R. Sudhölter Technische Universiteit Delft
Prof. dr. ir. J.W.M. Noordermeer Universiteit Twente
Prof. dr. ir. S. van der Zwaag Technische Universiteit Delft
Dr. ir. K.M.B. Jansen Technische Universiteit Delft

Copyright © 2015 by Z. Liu
Printed by Ipskamp Drukkers

All rights reserved. No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without the prior permission of the author.
# Contents

1 Introduction  
1.1 Self-healing materials 2  
1.2 Idealities and realities 3  
1.3 Modes of damages 4  
1.4 Rheology 6  
1.4.1 Mechanical analogs 8  
1.4.2 Self-healing related applications 13  
1.5 Halpin-Tsai mechanical model and its derivatives 14  
1.6 Future perspectives towards self-healing 16

2 Supramolecular elastomer polyborosiloxane: The synthesis and characterization 19  
2.1 Introduction 20  
2.2 Experimental Section 22  
2.2.1 Chemicals 22  
2.2.2 Modification and sampling 22  
2.2.3 Characterization 23  
2.3 Results and Discussion 24  
2.3.1 Thermal stability of anhydrous PDMS 24  
2.3.2 Synthesis of PBSs from PDMS and BA; observation of Si–O–B and B–O–B moieties 27  
2.3.3 The molecular weight distribution and its evolution during the modification reaction 31  
2.3.4 Development of mechanical properties upon modification 36  
2.4 Conclusions 38
3 The multifarious reversible cross-links in polyborosiloxane

3.1 Introduction
3.2 Experimental section
  3.2.1 Materials
  3.2.2 Methods
3.3 Results and discussion
3.4 Conclusions

4 Self-healing nanocomposites. A interpenetrated molecule-filler network leads to a separation of time-scale

4.1 Introduction
4.2 Experimental
  4.2.1 Chemicals
  4.2.2 Sampling
  4.2.3 Characterization
4.3 Results and Discussion
4.4 Conclusions

5 Tuning the mechanical properties of a supramolecular elastomer by incorporation of graphene oxide and organically modified graphene oxide

5.1 Introduction
5.2 Experimental section
  5.2.1 Materials
  5.2.2 Organo-modification of graphene oxide
  5.2.3 Methods
5.3 Results
  5.3.1 Characterization of GO and OMGO
  5.3.2 The formation of thixotropic nanocomposites due to the incorporation of GO
  5.3.3 The ordinary reinforcing effect of OMGO platelets
5.4 Discussion
5.5 Conclusions
6 A brief overview: the influence of filler morphology on the performance of Polyborosiloxane based self-healing nanocomposites. 85

6.1 Introduction 86
6.2 Chemicals 87
6.3 Methods 88
6.4 Results and Discussion 88
   6.4.1 0D filler incorporated composites 89
   6.4.2 1D multi-wall CNT incorporated nanocomposites 90
   6.4.3 2D clay and its derivatives incorporated nanocomposites 92
6.5 Conclusions 94

Summary 113

Samenvatting 115

Curriculum Vitae 118

Published Work 119

Acknowledgments 120
Introduction
1.1 Self-healing materials

Self-healing as a substantively scientific term was firstly introduced in the field of medical science in early 1920s\textsuperscript{1}. One of the definitions of self-healing is, the ability to repair damage and restore lost or degraded properties or performance using resources inherently available to the system\textsuperscript{2}. By 1969, a Nylon yarn reinforced self-healing concrete was patented and this was the first scientific record of a self-healing engineering material\textsuperscript{3}. The idea of self-healing materials originates from biological systems, where self-healing spontaneously and autonomously takes place without any human intervention. Self-healing of materials relies either on the use of added healing-agents, such as solvents, adhesives, catalysts, etc\textsuperscript{2,4,5,6,7,8,9,10}, or on the reversible cross-links at the molecular level\textsuperscript{2,11}.

Damage, fatigue and failure are the expected consequences of any naturally appearing or artificially manufactured substances. Thus, labour, energy and other resources are required for frequently repairing and replacing these expendables. The self-healing concept may yield safer, longer-lasting, fault-tolerant products, as well as a less pollutive, more sustainable and friendly living environment.

Self-healing materials (SHM) can be divided in different categories based on their compositions. A SHM that heals by means of consuming embedded healing agents or involving external stimuli is denoted "extrinsic SHM". Its counterpart is denoted "intrinsic SHM", which heals through rebuilding the interactions between the constituent molecules.

More specifically, embedded healing agents may be contained in "capsule" or in "vascular" systems. These represent two distinct filler morphologies. A healing agent that is stored will be released upon failure of the capsules or vessels. A capsule–system consists of isolated capsules, which are distributed isotropically or oriented in some special way. As referred to the polymer composites, spherical and cubic particles are sometimes defined as zero dimensional (0D) inclusions\textsuperscript{12,13}, but sometimes defined as 3D inclusions\textsuperscript{14}. Rod-like and planar particles are consistently denoted zero 1D and 2D inclusions\textsuperscript{12,13}, respectively. A vascular–system is more complicated as compared to a capsule-system, because a 3D vascular framework
stores and transports healing agents. As paybacks, a vascular–system may not only repair a macroscopic damage due to its transportable healing agent, but also heal microscopic cracks for multiple times, as long as a fracture does not occur at exactly the same spot as a previous one. Regarding the diverse healing mechanisms, the healing agent may be a solvent\textsuperscript{10,15}, a cross-linker, an adhesive\textsuperscript{16,17}, a catalyst\textsuperscript{4,18,19,20}, bacteria\textsuperscript{21}, etc.

In intrinsic systems, self-healing occurs without employing the added healing agents. Therefore it avoids integration and compatibility related problems. Such inherent self-healing material commonly relies on the reversible reactions\textsuperscript{22,23,24,25}, dispersed thermoplastic polymers (adhesives)\textsuperscript{26,27,28}, ionomic cross-links\textsuperscript{29,30,31,32}, molecular diffusion\textsuperscript{33,34,35,36,37,38}, supramolecular polymeric features\textsuperscript{39,40,41}, etc. However, heat or intense photo-illumination is required to trigger self-healing in the first four cases, which make their healing performance less autonomous.

In 2007, Prof. van der Zwaag edited the first comprehensive overview on self–healing materials, covering polymeric, metallic, ceramic and concrete composites\textsuperscript{42}. It has provided the community with a bright perspective, as such bio-inspired behavior can be applicable in most types of engineering materials.

In addition to recovering integrity and appearance, self-healing aims at restoring the designed functionality as well. In other words, self-healing mends the damages, as well as postpones failures. For instance, a load-bearing material may fail due to macroscopic damages or a gradual mechanical deterioration (fatigue). Embedding self-healingness in combination with an appropriate filler reinforcement may stop the development of cracks and heal them in-situ. Another application of the self-healing concept is to prevent corrosion, such as in paints, wire-cover, etc\textsuperscript{43,44,45,46}.

1.2 Idealities and realities

An ultimate and ideal self-healing material should be capable of autonomously and completely recovering its original appearance and functionality for an infinite number of cycles, without external stimuli or human intervention.
In capsule- and vascular- systems, a bio-inspired self-healing process is employed, where the preserved healing agents resemble stem-cells\textsuperscript{47} and will be autonomously transported, differentiated and consumed to heal fractures upon triggering. Intrinsic self-healing relies mainly on mobility and reversible cross-links between the constituent molecules.

However, challenges to the bio-inspired self-healing process are: 1) healing agents may be depleted near the healed positions, 2) preparation of capsules and vascular-frameworks, 3) suitability of healing agents for a certain matrix, and 4) shelf-life of healing agents. While for the intrinsic self-healing systems, people have to face the chemical stability of molecules and the weak mechanical performance.

Although in principle, every substance is visco-elastic and therefore is self-healable, a low healing efficiency limits the application. For instance, a broken thermoplastic may start self-healing, as soon as all the broken pieces are assembled together. However, it may take years to completely recover its inherent properties, because such healing is governed by diffusion and re-entanglement of molecules. Insignificant entanglement results in a visible "scar", which in industry is denoted "weld line" and represents a weak spot\textsuperscript{48}. Heating is one of the external stimuli, which will significantly increase the mobility of polymeric molecules and healing efficiency, especially when it goes above the glass transition temperature (T\textsubscript{g}). Recycling and reprocessing may recover this product, but at an even higher expense.

1.3 Modes of damages

Depending on the loading conditions, self-healing systems may damage mainly in the form of quasi-static fracture, impact\textsuperscript{49}, and fatigue\textsuperscript{2,50}. Specific techniques that were employed in characterizing self-healingness are double-cantilever beam (DCB), tapered double-cantilever beam (TDCB)\textsuperscript{6}, compact tension (CT)\textsuperscript{26}, single-edge notched beam (SENB)\textsuperscript{28}, three (four)-point bending\textsuperscript{51,52,53}, and double cleavage drilled compression (DCDC)\textsuperscript{23}.

Quasi-static fracture includes tearing\textsuperscript{16}, cutting\textsuperscript{36}, matrix-fiber delamination\textsuperscript{54},
transverse/shear cracking\textsuperscript{55}, etc. Quasi-static fracture experiments are employed in developing and characterizing self-healing polymer systems, because of the controllable and predictable crack propagation and crack size, as well as the quantifiable fracture parameters.

Out of plane impact may cause damage in different forms, including puncture, delamination, and mixed-mode cracking. Compression-after-impact (CAI) test\textsuperscript{56} is the common technique used for quantifying the restoration of compressive strength, in other words the self-healingness. Indentation is a special form of impact failure causing more localized damage. The ratio of the flexural testing results of the damaged (healed) to virgin specimens is used for quantifying self-healingness.

Fatigue tests are used to simulate dynamic failure. Fatigue damage is governed by frequency, direction, and amplitude of the applied stress, as well as the inherent mechanical properties of the material. The parameter that represents the self-healingness against fatigue loading is denoted the fatigue life extension, $\lambda$.

$$\lambda = \frac{N_{\text{healed}} - N_{\text{control}}}{N_{\text{control}}},$$

where, $N$ is the fatigue life of a material. The subscripts refer to specific healing conditions, such as temperature, time, pressure, humidity, etc\textsuperscript{19,20}.

An optimal self-healing system should be able to recover at least at the same rate as the damage rate, in order to maintain material stasis. However, the majority of currently existing self-healing systems heals slower than the damage rate, which leads to an accumulation of damage. Therefore, the self-healing efficiency (Eq. 1.2)\textsuperscript{2} may vary depending on healing conditions, such as temperature, compression, time, humidity, etc. In Eq. 1.2, $\eta$ represents the healing efficiency, $f$ is the property of interest under different healing conditions. $f_{\text{damaged}}$ is usually set zero, as it possesses no fracture resistance in the damaged state.

$$\eta = \frac{f_{\text{healed}} - f_{\text{damaged}}}{f_{\text{virgin}} - f_{\text{damaged}}}. $$

(1.2)
1.4 Rheology

A technique that has been applied throughout this project and played an essential role is rheology. Rheology reveals the nature of viscoelastomers by means of showing the frequency dependent mechanical performance, where viscosity and elasticity respectively dominate in the low and high frequency domains.

A rheometer may be operated under various circumstances, such as steady state, oscillatory, squeeze and pull, etc. The oscillatory measurements are carried out in either a stress-driven or a strain-driven mode. In other words, a rheometer can stimulate the sample with an oscillating stress and measuring the oscillating strain as a response, or vice versa.

\[
e(t) = \varepsilon_0 \sin(\omega t).
\] (1.3)

Equation 1.3 gives the oscillatory strain \( \varepsilon \) as an example of the input signal, where \( \varepsilon_0, \omega \) and \( \sin(\omega t) \) represent the amplitude, oscillating frequency and wave form of the input strain. The responding stress \( \sigma \) of a purely elastic solid is proportional to the strain,

\[
\sigma(t) = \kappa \varepsilon_0 \sin(\omega t).
\] (1.4)

Differently, the responding stress of a purely viscous fluid is proportional to the strain rate,

\[
\sigma(t) = \eta \varepsilon_0 \omega \sin(\omega t + \pi/2).
\] (1.5)

\( \kappa \) and \( \eta \) are the elastic and viscous constants of the materials. We see an obvious phase lag in the above mentioned two extremes, \( \pi/2 \), because a purely elastic solid can immediately respond to the stimulus. However, a purely viscous fluid can not.

In reality, none of these two extremes exists, as all the materials behave as viscoelastomers. The retardation of different systems is distinct, which is normally given as a phase difference \( \delta \). Replacing the term \( \eta \varepsilon_0 \omega \) and \( \pi/2 \) respectively with the stress amplitude \( (\sigma_0) \) and \( \delta \), Eq. 1.5 can be generalized into Eq. 1.6, to describe the responding stress of any viscoelastomer.

\[
\sigma(t) = \sigma_0 \sin(\omega t + \delta).
\] (1.6)
Rewriting Eq. 1.6 according to trigonometry, we see the stress becomes the sum of in phase response and out-of phase response (Eq. 1.7).

\[ \sigma(t) = \sigma_0 \cos(\delta) \sin(\omega t) + \sigma_0 \sin(\delta) \cos(\omega t). \] (1.7)

For a subject with an original dimension, \( l \), which is deformed under the above mentioned oscillatory stress via a contact area, \( a \), the differentiated displacement is obtained by differentiating Eq. 1.3 with respect to \( t \),

\[ d\Delta l(t) = l \varepsilon_0 \omega \cos(\omega t) dt. \] (1.8)

Regarding the force applied on this object, where \( a \) represents area,

\[ F(t) = a \sigma(t) = a \sigma_0 \cos(\delta) \sin(\omega t) + a \sigma_0 \sin(\delta) \cos(\omega t), \] (1.9)

the work that was done in this time interval is

\[ F(t)d\Delta l = l \varepsilon_0 \omega F(t) \cos(\omega t) dt. \] (1.10)

Integrating the work in a complete cycle, it gives

\[ W = a \pi \varepsilon_0 \sigma_0 \omega \sin(\delta). \] (1.11)

However, Eq. 1.11 only represents the viscous properties of this subject, as the elastic part only restores the energy and will respond without energy dissipation. Equation 1.11 describes the energy loss in an oscillatory cycle, therefore, the out-of-phase component is also denoted "loss component". Similarly, the in-phase component describes the storage properties. We can express both the in-phase and out-of-phase components in a comprehensive complex equation, by means of applying the Euler’s relation (Eq. 1.12).

\[ e^{ix} = \cos(x) + i \sin(x). \] (1.12)

So complex strain \((\varepsilon^*)\) and stress \((\sigma^*)\) are given in Eq. 1.13 and Eq. 1.14,

\[ \varepsilon^* = \varepsilon_0 e^{i\omega t} = \varepsilon_0 \cos(\omega t) + i \varepsilon_0 \sin(\omega t). \] (1.13)
\[ \sigma^* = \sigma_0 e^{i(\omega t + \delta)} = \sigma_0 \cos(\omega t + \delta) + i\sigma_0 \sin(\omega t + \delta). \quad (1.14) \]

The ratio of the stress (\(\sigma^*\)) and strain (\(\varepsilon^*\)) is denoted the "modulus", in Eq. 1.15. It describes the mechanical properties of a given subject in a very easily understood sense as, the stress needed for causing a unit strain.

\[ G^* = \frac{\sigma^*}{\varepsilon^*}. \quad (1.15) \]

We combine Eq. 1.13 and Eq. 1.14, then Eq. 1.15 is rewritten as

\[ G^* = \frac{\sigma^*}{\varepsilon^*} = \frac{\sigma_0 e^{i(\omega t + \delta)}}{\varepsilon_0 e^{i\omega t}} = \frac{\sigma_0 \cos(\omega t + \delta) + i\sigma_0 \sin(\omega t + \delta)}{\varepsilon_0 \cos(\omega t) + i\varepsilon_0 \sin(\omega t)} = \frac{\sigma_0}{\varepsilon_0} \left[ \cos(\omega t + \delta) \cos(\omega t) + \sin(\omega t + \delta) \sin(\omega t) \right] + i \frac{\sigma_0}{\varepsilon_0} \left[ \sin(\omega t + \delta) \cos(\omega t) - \cos(\omega t + \delta) \sin(\omega t) \right] = \frac{\sigma_0}{\varepsilon_0} \cos(\delta) + i \frac{\sigma_0}{\varepsilon_0} \sin(\delta). \quad (1.16) \]

\(G^*\) is commonly referred to as the complex dynamic modulus, \(G'\) and \(G''\) are used to represent the real part and imaginary part, and denoted respectively as the storage modulus and loss modulus (Eq. 1.17).

\[ G^* = G' + iG'' \quad (1.17) \]

### 1.4.1 Mechanical analogs

The mechanical analogs corresponding to the most simple viscoelastic fluid is a linear combination of a spring (purely elastic) and a dashpot (purely viscous). Figure.1.1 shows these two basic elements, as well as a few simple integrated units by means of grouping these elements in some simple orders.
As a purely elastic object (Fig. 1.1 (a)), the spring instantaneously deforms proportionally to the applied stress (Eq. 1.18, Hooke’s Law). While, in the case of a purely viscous subject (Fig. 1.1 (b)), the corresponding stress is proportional to the strain rate, $\dot{\gamma} = d\varepsilon/dt$, as given in Eq. 1.19

$$\frac{d\varepsilon}{dt} = \frac{1}{G} \frac{d\sigma}{dt}, \quad (1.18)$$

$$\sigma = \eta \frac{d\varepsilon}{dt}, \quad (1.19)$$

where $G$ and $\eta$ represent the characteristic elasticity and viscosity of the spring and dashpot, respectively.

Figure 1.1 (c) shows a linear combination of a spring and a dashpot, which results in a Maxwell unit. In a Maxwell unit, the stress in the dashpot and spring is identical, but the total strain will be the sum of each, Eq. 1.20.


\[ \frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{G} \frac{d\sigma}{dt}. \]  

(1.20)

When such Maxwell unit is subject to a constant stress, \( \sigma_0 \), the resulting strain becomes a function of time as shown in Eq. 1.21. The spring reacts spontaneously and results in a sudden strain, \( \sigma_0/\eta \). The dashpot will then gradually and linearly increase the strain. The sudden strain due to the spring is the recoverable strain, if \( \sigma_0 \) is removed.

\[ \varepsilon(t) = \frac{\sigma_0}{G} + \frac{\sigma_0 t}{\eta}. \]  

(1.21)

The creep modulus according to Eq. 1.15 is written as

\[ G(t) = \frac{\sigma_0}{\varepsilon(t)} = \frac{G\eta}{\eta + Gt}. \]  

(1.22)

The creep compliance \((J(t))\) is the ratio of the strain over the applied stress. Clearly, the creep compliance is the inverse of the creep modulus.

\[ J(t) = \frac{\varepsilon(t)}{\sigma_0} = \frac{\eta + Gt}{G\eta} \]  

(1.23)

If the Maxwell unit is subject to a sudden constant strain, \( \varepsilon_0 \), the spring will also immediately respond with a stress, \( \sigma_0 = \varepsilon_0 G \). However, the gradual deformation in dashpot will relax the stress on the spring over time. Equation.1.24 indicates that the constant strain will cause an instant stress, which relaxes exponentially with a time constant of \( \tau = \eta/G \). This time constant is denoted characteristic terminal relaxation time.

\[ \sigma(t) = \sigma_0 e^{-\frac{Gt}{\eta}} = \sigma_0 e^{-\frac{t}{\tau}} \]  

(1.24)

With an oscillatory stimulus, \( \sigma(\omega) \) or \( \varepsilon(\omega) \), the solution of Eq. 1.20 provides the complex dynamic modulus of the Maxwell unit. Here we do not repeat the complicated algebraic efforts and the Laplace transformation, which were discussed in great details by Banks, et al.\textsuperscript{57}, but directly present the solutions in Eq. 1.25.

\[ G^* = \frac{\sigma_0}{\varepsilon_0} e^{i\delta} = \frac{G(\eta\omega)^2}{G^2 + (\eta\omega)^2} + i \frac{G^2\eta\omega}{G^2 + (\eta\omega)^2}. \]  

(1.25)
The specific angular frequency, at which $G''$ reaches its maximum, inversely equals to the terminal relaxation time, $\tau = \eta/G$.

$$G' = \frac{G(\eta \omega)^2}{G^2 + (\eta \omega)^2}, G'' = \frac{G^2 \eta \omega}{G^2 + (\eta \omega)^2}. \quad (1.26)$$

Figure.1.1 (d) corresponds to the Kelvin-Voigt (KV) model, in which a spring is connected with a dashpot in parallel. In this model, the strain in each loop is identical, but the total stress equals to the sum of both paths (Eq. 1.27).

$$\sigma = G\epsilon + \eta \frac{d\epsilon}{dt}. \quad (1.27)$$

Such combination emphasizes that the system will eventually stop displacing owing to the presence of the spring. Equation.1.28 gives the evolution of strain under a constant stress. It says that such constant stress drives the system to deform exponentially towards a maximum, $\sigma_0/G$. The removal of such stress will lead to a completely removal of strain, in other words, a total recovery.

$$\epsilon(t) = \frac{\sigma_0}{G} (1 - e^{-\frac{G}{\eta}t}) \quad (1.28)$$

When the KV unit is subject to a constant strain, the spring will bear an unrelaxable stress that equals to $G\epsilon$, Eq. 1.29.

$$\sigma = G\epsilon \quad (1.29)$$

The real and imaginary parts of the complex dynamic modulus are given in Eq. 1.30 and Eq. 1.31, respectively.

$$G' = G. \quad (1.30)$$

$$G'' = \eta \omega. \quad (1.31)$$

Figure.1.1 (e) shows a more complicated combination of the basic elements. The Maxwell arm is connecting with a separate spring in parallel. Such combination is denoted the standard linear solid (SLS) model, or three-parameter model. In this model, there are four equation stating the balance of stress and strain in stead of two, as compared with the above mentioned simple ones. Two equations are still
describing the stress and strain balance in the Maxwell arm, meanwhile, two more equations establish the overall stress and strain balance. Equations 1.32 ~ 1.35 show the four balance equations as,

\[
\sigma_{\text{total}} = \sigma_{S2} + \sigma_m,
\]

(1.32)

\[
\varepsilon_{\text{total}} = \varepsilon_{S2} = \varepsilon_m,
\]

(1.33)

\[
\sigma_m = \sigma_{S1} = \sigma_{D1},
\]

(1.34)

\[
\varepsilon_m = \varepsilon_{S1} + \varepsilon_{D1}.
\]

(1.35)

where subscripts, S1, S2 and D1 represent the spring and dashpot in the Maxwell arm. Meanwhile, Eq. 1.32 and 1.33 can also be written as,

\[
\dot{\sigma}_{\text{total}} = \dot{\sigma}_{S2} + \dot{\sigma}_m = \dot{\sigma}_{S2} + \dot{\sigma}_{S1} = G_2 \dot{\varepsilon}_{S2} + \dot{\sigma}_{S1},
\]

(1.36)

\[
\dot{\varepsilon}_{\text{total}} = \dot{\varepsilon}_{S2} = \dot{\varepsilon}_m = \frac{\dot{\sigma}_{S1}}{G_1} + \frac{\sigma_{S1}}{\eta}.
\]

(1.37)

The expression of the overall stress balance can be obtained by embedding Eq. 1.36 and 1.37 into Eq. 1.32\textsuperscript{58}, as

\[
\sigma_{\text{total}} = G_2 \varepsilon_{\text{total}} + \eta \dot{\varepsilon}_{\text{total}} - \frac{\eta}{G_1} \dot{\sigma}_{S1}
\]

(1.38)

\[
= G_2 \varepsilon_{\text{total}} + \eta \dot{\varepsilon}_{\text{total}} - \frac{\eta}{G_1} (\dot{\sigma}_{\text{total}} - G_2 \dot{\varepsilon}_{S2}).
\]

We rearrange Eq. 1.38 and the final expression is given in Eq. 1.39 as,

\[
\sigma_{\text{total}} = G_2 (\varepsilon + \tau_m \frac{d\varepsilon}{dt}) - \tau_r \frac{d\sigma}{dt},
\]

(1.39)

where, the characteristic terminal relaxation time, \(\tau_m\), and the retardation time constant, \(\tau_r\), in the SLS model are given below in Eq. 1.40 and 1.41, respectively.

\[
\tau_m = \frac{\eta_1}{G_1}.
\]

(1.40)
\[ \tau_r = \eta_1 \frac{G_1 + G_2}{G_1 G_2}. \]  

(1.41)

Similarly, the formulas that are related to the creep, recovery and stress relaxation processes can be easily obtained. For example, \( \varepsilon(t) \) in the creep process can be obtained by setting the \( d\sigma/dt \) in Eq. 1.39 to be 0, and solve the differential equation as in Eq. 1.42,

\[ \varepsilon(t) = \frac{\sigma_0}{G_2} - \frac{\sigma_0 G_1}{(G_1 + G_2) G_2} e^{-\frac{t}{\tau_r}}. \]  

(1.42)

The stress relaxation process can be obtained by setting the \( d\varepsilon/dt \) term to by 0, and solve the remaining differential equation as in Eq. 1.43

\[ \sigma(t) = \frac{\sigma_0}{G_1 + G_2} \{ G_2 + G_1 e^{-\frac{t}{\tau_m}} \} \]  

(1.43)

The storage and loss modulus are given in Eq. 1.44 and 1.45, respectively.

\[ G' = \frac{G_2 (1 + \tau_r \tau_m \omega^2)}{1 + (\tau_m \omega)^2} \]  

(1.44)

\[ G'' = \frac{G_2 (\tau_r - \tau_m) \omega}{1 + (\tau_m \omega)^2} \]  

(1.45)

There are plenty of much more complicated models, such as: 1) the four-parameter SLS model, where an extra parameter, \( 0 < \alpha < 1 \), can be used to account for the peak broadening\(^{59} \) and renders the original SLS model when \( \alpha = 1 \); 2) the generalized Maxwell model, in which a number of Maxwell units are connected in parallel; 3) the generalized SLS model, where a separate spring connects in parallel with a number of in parallel connected Maxwell models; etc.

### 1.4.2 Self-healing related applications

Apart from identifying the response of a material under shear deformation as a whole, the rheometer is also applicable in measuring the cohesive properties of a sample. Such cohesive properties are in fact a measure of the self-healingness. The protocol is to cast a thin film of a sample onto the lower plate of the rheometer, meanwhile another film with known thickness from the same sample is glued onto the upper plate.
These two films can be controlled to move towards each other, contact at tunable conditions (temperature, time, humidity, indentation, etc), and then pull apart. The stress-strain relation during the pulling process can be used to represent the cohesive properties under controlled contacting conditions. With this approach, we can determine the minimal contacting time for self-healing, and the evolution of the recovered properties (Young’s modulus) as a function of contacting time, temperature, humidity, etc.

Our initiative of applying this approach is to find the correlation between the minimal contacting time in the self-healing process and the terminal relaxation time in the oscillatory measurements.

1.5 Halpin-Tsai mechanical model and its derivatives

The Halpin-Tsai mechanical model is a well-known equation that has been long used to describe filler reinforced composite systems. It not only takes the filler geometry into account, but also indicates the orientation and dispersion of filler particles in bulk by a shape factor. Equation 1.46 shows the Halpin-Tsai model in the generalized form \( E^*, E^*_m, E_f \) are the modulus of the composite, matrix, and filler particle. The former two are given in a complex form, however the loss part of the filler is usually ignored. \( \xi \) and \( \theta \) represent the shape factor and the volume fraction of filler particles, respectively.

\[
\frac{E^*_c}{E^*_m} = \frac{1 + \xi \eta \theta}{1 - \eta \theta}, \text{ in which, } \eta = \frac{E_f}{E_m} \frac{E^*_f - 1}{E^*_f - \xi}
\]  

(1.46)

The shape factor \( \xi \) relies on the geometry and orientation of filler particles, as well as on the direction of applied stress. The formulas of the shape factor with respect to the applying conditions are summarized as follows:

1. For 0D spherical particles
   \( \xi = 1.5 \) or 2, regardless the direction of stress.

2. For 1D parallel rods and fibers (\( l: \) length, \( d: \) diameter.)
   \( \xi = 2(l/d) \), if the stress is along the fibre direction.
   \( \xi = 2 \), if the stress is applied perpendicularly to the fiber direction.
3. For 2D parallel platelets (w: width, t: thickness.)

\[ \xi = 2(w/t) \], if the stress is in the radial direction of platelets.

\[ \xi = 2 \], if the stress is applied perpendicularly to the platelets (transverse).

The Halpin-Tsai model is often modified with respect to the specific filler geometry and orientation, which can be determined prior to the fitting procedure, by applying wide angle X-ray diffractometry (WAXD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), etc.

If the filler particles are isotropically oriented, then the Halpin-Tsai model can be modified accordingly to the filler geometry. Equation 1.47 gives the specified Halpin-Tsai model for randomly oriented fiber reinforcements. The additional factor \( \phi_{\text{max}} \) represents the maximal packing fraction of the fibers, and is taken as \( \phi_{\text{max}} = 0.82 \).

\[
\frac{E_c^*}{E_m^*} = \frac{1 + \xi \eta \theta}{1 - \eta \psi \theta}, \text{ in which, } \psi = 1 + \left( \frac{1 - \phi_{\text{max}}^2}{\phi_{\text{max}}^2} \right) \theta
\]  

(1.47)

For randomly oriented 2D platelets, an empirical expression is used as below,

\[ E_c^* = \beta_{||} E_{c||} + \beta_{\perp} E_{c\perp}. \]  

(1.48)

In Eq. 1.48, \( E_{c||} \) and \( E_{c\perp} \) account for the parallel and transverse moduli, where \( \xi = 2w/3t \) and \( \xi = 2 \) are applied in calculating \( E_{c||} \) and \( E_{c\perp} \), respectively. \( \beta_{||} \) and \( \beta_{\perp} \) are determined empirically as \( \beta_{||} = 0.49 \) and \( \beta_{\perp} = 0.51 \).

At high volume fraction of filler, the Halpin-Tsai model itself can no longer predict the performance of the nanocomposites, due to the formation of a filler network. The tensile modulus of the network (\( E_N^* \) in Eq. 1.49) can be estimated to be proportional to the product of the volume fraction of filler, the number of contacts between particles, and the energy of the particle–particle interaction. Thus, the original Halpin-Tsai model together with the network contribution (Eq. 1.49) can reasonably estimate the mechanical performance of the nanocomposites of high-volume-fraction of filler particles.

\[ E_c^* = E_{HT}^* + E_N^*. \]  

(1.49)
In this thesis, we will mostly focus on the frequency-dependent mechanical properties of our materials in their linear viscoelastic regimes. We have realized that the intrinsic self-healing matrix is an almost perfect Maxwell fluid within the frequency window of the rheometer. However, the filler reinforced self-healing nanocomposites may exhibit a wide variety in performances, for instance: 1) the behavior of nanocomposites deviates from a typical Maxwell fluid towards a viscoelastic solid due to the formation of filler network; 2) the particle-molecule interaction may slow down the self-healing by lowering the number density of reversible cross-links between polymer molecules; 3) the particle-molecule interaction is some specific cases may soften and eventually liquefy the composite, because the strong molecule-molecule cross-links are largely replaced by the weak particle-molecule hydrogen-bonds; etc.

Regarding to our unique self-healing matrix material, the inclusion of filler particles can be increased to a surprisingly high mass fraction (~0.7 for the commercial nano clay), the formation of a particle network becomes un-avoidable. In the mechanical analogs, we can represent the filler network with a separate spring, connecting in parallel to a Maxwell arm, which represents our viscoelastic self-healing matrix. Then such mechanical analog is transformed into a SLS model.

The use of Halpin-Tsai model in fact can provide us with reasonable prediction on filler orientation, although it is not very suitable to composites at high filler concentrations. Regarding to Halpin-Tsai model, the shape factor of a composite will generally be constant at low filler content, but start decreasing above a certain threshold. This is due to the insufficient intercalation of particles. However, we sometimes see an increasing shape factor above the threshold, which implies the formation of filler network in practice. We will discuss the performance of Halpin-Tsai model with those models that are based on the mechanical analogs in Chapter 4.

1.6 Future perspectives towards self-healing

In 2009, Anderson, et al., have introduced the formation of a nanoscale DNA box. The lid of this box can be open and closed in a well-controlled manner. It can be an outstanding remark for the capsule— and especially for the vascular—systems. It may
trigger the development of the self-healing vessels, which may self-assemble after releasing healing agents in the presence/absence of photo/thermal agitation, air, etc. If the vessels can close and keep transporting the healing agent, then self-healing can be expected for multiple times even when fractures all occur at the same spot.

Meanwhile, efforts have been spent on reinforcing the mechanical performance of the intrinsic self-healing systems. Quite a few ureidopyrimidinone (UPy) based self-healing polymers resist gravity due to the highly self-organized hydrogen-bonding pairs. Metal coordination bonding is also proved to be a promising route.

In this thesis, we have designed, prepared and characterized a class of advanced intrinsic self-healing polymer nanocomposites, where the self-assembled filler skeleton is immersed in the continuous phase of the supramolecular elastomer. The skeleton that interpenetrates through the polymer matrix not only prevents the supramolecular elastomer from flowing, but also makes the nanocomposite more load-bearing. The supramolecular elastomer is responsible for integrating the two-component nanocomposite as a whole with its reversible intermolecular cross-links. By tuning the particle-molecule adhesion, we are able to obtain a load-resistant nanocomposite without prolonging the healing time.
2

Supramolecular elastomer polyborosilxoane: The synthesis and characterization

This chapter is for a large part based on:

2.1 Introduction

Polyborosiloxanes (PBSs), which were invented initially in the search for substitutes of natural rubbers, possess reversible physical cross-links. A material like PBS may be denoted a supramolecular elastomer\textsuperscript{11,39,72,73}. PBS products are known under the names, Silly Putty, bouncing putty\textsuperscript{74}, Solid-liquid\textsuperscript{75}, dilatant compound\textsuperscript{76}, etc. In all commercial applications, PBS constitutes the viscoelastic matrix, and inorganic/organic fillers are added for different engineering applications or lowering cost\textsuperscript{77}. At room temperature, pure PBSs behave elastically under a rapid strain variation, and suffer from brittle fractures. However, on longer time-scales, they flow as a viscous fluid. The fascinating viscoelastic properties made PBSs applicable in education on various deformation processes\textsuperscript{74}, in tectonic modeling of the slow deformation of rocks\textsuperscript{76}, as cleaning adhesive, as solvent in zero-gravity chemistry\textsuperscript{78}, as additive in processing technique\textsuperscript{79}, in insulating coating film for electric wires\textsuperscript{80}, for LED encapsulation as light and heat resistant materials\textsuperscript{80}, etc.

Recipes for synthesizing PBS have been published by McGregor\textsuperscript{81}, Wright\textsuperscript{77}, Zinchenko\textsuperscript{82}, and Vale\textsuperscript{83}. The goal is to create abundant hydroxyl groups in the siloxane chains via the boric acid (BA) modification. The first three recipes are based on modification of polydimethylsiloxane (PDMS) in the presence of BA above 150 °C, where BA facilitates the chain cleavage by grafting to the ends of the cut PDMS chains. Vale has developed two low-temperature dichlorodimethylsilane (DCDMS) based synthetic procedures. Upon releasing hydrogen chloride, PBS can be produced from DCDMS and BA either at 90 °C by condensation polymerization, or by solution polymerization in tetrahydrofuran (THF) as solvent and solid carbon dioxide as external coolant, respectively. Because of the convenience of synthetic work and purification, we elaborated on the hydrolytic route in this work. Heating a mixture of PDMS and BA above 150 °C will result in viscoelastic PBS\textsuperscript{77,81,82}. PBS possesses abundant borono end groups, Si−O−B(OH)\textsubscript{2}. The hydroxyl groups are the origin of hydrogen (H)-bonds that establish reversible cross-links. Besides the desired borono end groups, Zinchenko and coworkers\textsuperscript{82} also observed boroxane bonds, B−O−B, in the PBSs, which indicates some polymerization of BA. By quantifying the presence of different chemical groups with Proton Magnetic Resonance (PMR) and Infrared (IR) Spectroscopy, Zinchenko and coworkers inferred the coexistence of two more
molecular structures (Fig. 2.1, II and III), in addition to the target one (Fig. 2.1, I).

![Figure 2.1: The three possible molecular structures of the boric acid modified hydroxy terminated polydimethylsiloxane, proposed by Zinchenko and co-workers.](image)

Pristine PDMS possesses a low glass transition temperature in the range of -150 °C to -120 °C, because of the flexible siloxane backbone. Molecular mobility in combination with the reversible intermolecular interactions make PBS a candidate for a self-healing material. When PBS suffers cracks or fractures, just bringing the broken pieces together leads to spontaneous healing. Once traditional thermal plastics undergo failures, chopping and remoulding are necessary, otherwise the engineering performance along the fracture is not recovered due to the lack of chain entanglement and alignment. However, reversible cross-linking allows PBS based materials to fully recover without complicated reprocessing. Additionally, PBS based materials will leave no weld line after injection moulding.

In this chapter, we describe the modification process of PDMS to PBSs in terms of the evolution of the molecular weight distribution, and the simultaneous formation of Si–O–B moieties. The development of the molar mass distribution as well as the nature of formed moieties are characterized by a combination of gel permeation chromatography (GPC) and IR spectroscopy. As an important novel element, we
describe a refinement procedure, in which all chain ends are converted into borono, by hydrolyzing the boroxane bonds at humid conditions and subsequent removal of released boric acid. We characterized the molecular structure of the un-refined and refined PBSs by combining direct observation and Fourier transform infrared (FTIR) spectroscopy. Furthermore, the pronounced changes of mechanical properties upon increasing modification are investigated by dynamic rheometry.

2.2 Experimental Section

2.2.1 Chemicals

Trimethylsiloxy terminated linear Polydimethylsiloxane (PDMS) 100k (ABCr GmbH & Co.KG, Karlsruhe, Germany.), and boric acid (BA) BP168-1 (Acros Organics BVBA, Geel, Belgium.) were purchased for the synthesis of polyborosiloxanes (PBSs). The molar mass of "PDMS 100k" was not supplied, only a value of kinematic viscosity of 100,000 cSt. We determined number and weight average molar mass, \( M_n \) and \( M_w \), by means of gel permeation chromatography (GPC), see Table. 2.1. Hexane of reagent plus grade (Sigma-Aldrich) and tetrahydrofuran (THF) of HPLC grade (Acros), served as solvent for purification and as eluent for GPC measurements. Mono-disperse PDMS standards (PSS GmbH) were used to calibrate the GPC.

2.2.2 Modification and sampling

PDMS and BA were dried at 50 °C in a vacuum oven overnight before use. A mixture of PDMS and BA at weight ratio of 10:1 was pre-mixed by an overhead stirrer, and then heated in a heating mantle. A temperature controller and a thermo-couple constituted a controllable heating unit together with the heating mantle, where the temperature controller tuned the temperature by receiving the sample temperature from the thermo-couple. The beginning of the modification was defined as the moment, at which the heating unit was switched on. The sample temperature reached 200 °C within 15 minutes.

During the reaction, we observed abundant condensed water vapor released from the reaction mixture. Samples of the intermediate products (PBSs) were collected once per hour. Synthesis was halted after about 6 hours, because at that stage the
product was too viscous to be stirred. The intermediate samples were all solid after cooling. To remove the un-reacted BA and other possible contaminations, raw PBSs were dissolved in hexane and filtered (pore size of the filter paper was about 200 nm).

We noticed that some white sediment may again appear in the filtrate if we keep it under air for a few days. After 6 resting/filtering cycles, the filtrate no longer had visible contamination.

Transparent and colorless elastomers were obtained upon evaporating the hexane at 70 °C and 0.6 bar. We will call this well-purified product "refined PBS" (rPBS) throughout this thesis. The product was stored at 50 °C in a vacuum oven for at least 10 hours before investigation. Anhydrous PDMS was processed in the same setup at 240 °C for 3 hours, in order to study its thermal stability. For easy referring, samples are named as shown in Table. 2.1.

2.2.3 Characterization

Gel Permeation Chromatography (GPC) measurements were done using a Shimadzu Prominence GPC system, equipped with a Shodex LF-804 column. Tetrahydrofuran (THF) for HPLC served as the eluent at a flow rate of 1 ml/min at 40 °C. Correlation between the retention time and the molar mass distribution (MD) was established, based on calibration using mono-disperse PDMS standards. Data that were acquired from the refractive index detector, were analyzed by using the LabSolutions software.

Fourier Transform Infrared (FTIR) Spectroscopy was performed with a Perkin-Elmer Spectrum 100 series FTIR spectrometer, using the attenuated total reflectance (ATR) mode. ATR is convenient, as liquid, films and fine powder, can be directly investigated.

Dynamic rheological measurements were carried out on a TA AR G2 Rheometer, using the plate-plate geometry: an upper plate of diameter of 40 mm for pristine Polydimethylsiloxane (PDMS), and a 8 mm plate for the PBSs, because of their much larger stiffness.
Dynamic Mechanical Analysis (DMA) was used to examine the glass transition temperature ($T_g$) of PBSs in 3-point bending mode. PBS that was modified for 6 hours was selected for this purpose, because it is expected to have the highest degree of modification, and therefore possesses the largest change of the $T_g$ compared to the raw PDMS. Samples for DMA measurement with dimensions 3 mm in thickness, 7 mm in width, and 15 mm in length were prepared via compression moulding at 120 °C. Liquid nitrogen was used to lower the temperature of the measuring unit.

2.3 Results and Discussion

2.3.1 Thermal stability of anhydrous PDMS

In order to investigate the thermal stability of anhydrous PDMS, it was exposed to a temperature of 240 °C for 3 hours. The reflective index (RID) of the heat treated PDMSs were measured by GPC at 40 °C in THF. The molar mass distribution of PDMS does not change significantly (see Fig. 2.2 (a)). However, the amplitude of the dynamic complex viscosity ($|\eta^*|$) slightly decreases over time (Fig. 2.2 (b)). This decreasing viscosity indicates that PDMS in fact slightly degrades, possibly due to some residual moisture. Figure 2.3 shows the infrared spectra of PDMS after exposure to 240 °C. Peaks in the range of 1020 - 1090 cm$^{-1}$ are assigned to vibrations of the siloxane backbone. Other bands (in cm$^{-1}$) assigned to groups and bonds are as follows: 880 and 1260 for $-\text{Si(CH}_3\text{)}_2$, and 2905 - 2960 for $-\text{CH}_3$. We observe that the band corresponding to the siloxane backbone slightly decreases over time, which indicates a small degree of backbone cleavage, in line with the rheological observations.
Figure 2.2: Molar mass distribution (MD) (a) and the amplitudes of the dynamic complex viscosity (b) of the pristine PDMS, which was subject to 240 °C for 3 hours. MD was measured at 40 °C in THF and rheology was measured at 20 °C.
Figure 2.3: FTIR spectra of pristine PDMS that was subject to 240 °C for 1 to 3 hours. The measurements were carried out under ATR mode at room temperature.
2.3.2 Synthesis of PBSs from PDMS and BA; observation of Si–O–B and B–O–B moieties

![FTIR spectra of PBSs and PDMS](image)

**Figure 2.4:** FTIR spectra of crystalline boric acid and the white powder collected in the refining step, (a). FTIR spectra of rPBSs and pristine PDMS, (b). The measurements were carried out under ATR mode at room temperature.
PBSs were prepared by reacting PDMS with BA at 200 °C, followed by purification. As mentioned in the experimental section, the filtered PBSs/hexane solution may turn from clear into cloudy again upon exposure to ambient humidity at room temperature. Repeated resting and filtering result in a clear and colorless filtrate, as well as a white powder on the other hand. PBS was collected by removing the hexane from the filtrate. The final product stayed crystal-clear and colorless under air. We call this product "refined PBS" (rPBS). We washed the white substance with hexane, and its FTIR spectrum showed large similarity with that of boric acid powder, as shown in Fig. 2.4 (a).

We compared the IR spectra of raw and refined PBSs in Fig. 2.4 (b), which helped explain the consecutive appearance of the white substance. Raw PBS collected immediately after the reaction was transparent and referred to as "PBS raw dry" due to the high reaction temperature and the long reaction time. Its IR spectrum (orange curve in Fig. 2.4 (b)) clearly demonstrated the presence of B–O–B moieties by the band at 1380 cm⁻¹. After keeping this product under air for a few days it became turbid "PBS raw". We notice that the B–O–B peak decreases, while a peak at 1150 cm⁻¹ that corresponds to the in-plane B–O–H bending of both trigonal and tetrahedral boron²⁸ increases (green curve in Fig. 2.4 (b)). We interpret these observations by the occurrence of polymerization of some BA and borono terminals during the reaction via condensation. Bulky boroxane ends that contain several boron atoms are thereby formed. Upon exposure to ambient humidity, these are hydrolyzed, leading to BA formation. Therefore, we conclude that the white material, which is formed from the raw PBSs is in fact boric acid released by hydrolysis of B–O–B bonds.

Refined PBSs were collected after 6 filtering/resting cycles, followed by removal of hexane. These visco-elastomers stayed crystal-clear and colorless. IR characterization (red curve in Fig. 2.4 (b)) indicates that B–O–B moieties have nearly vanished, Si–O–B bonding is unchanged. We conclude therefore that end groups resembling Fig. 2.1, II are all converted into borono ends (Fig. 2.1, I) upon refinement. For organo-boronic acids⁸⁹,⁹⁰,⁹¹, it is known that a dynamic condensation/hydrolysis equilibrium between borono terminals and boroxines is spontaneously established. Boroxine represents the structurally preferred cyclotrimeric anhydride of boronic acid⁹², while other anhydrides of boronic acid are generally called boroxane. It
is to be expected that the borono terminals of the PBSs behave similarly, and are involved in a condensation/hydrolysis equilibrium $(-\text{B(OH)}_2 \rightleftharpoons \text{B-O-B} + \text{H}_2\text{O})$ as well. An interesting prediction is that the rPBS yields a covalently cross-linked boroxane elastomer upon dehydration, and at humid conditions hydrolysis renders a supramolecular elastomer again.

The degree of modification of PDMS was also characterized by FTIR spectroscopy (see Fig. 2.5 (a)). Spectra of rPBSs are normalized according to peaks at 1260 cm$^{-1}$, which is assigned to the Si(\text{CH}_3)$_2$ structure that hardly changes during reaction. The band at 1340 cm$^{-1}$ that corresponds to the IR absorbance of Si–O–B moieties$^{93}$ increases over time. Such increase indicates that boron containing moieties are getting bonded to the cleaved PDMS, and that the degree of modification increases as the reaction proceeds. The increase of the absorbance by Si–O–B moieties with the reaction time is shown in Fig. 2.8 and will be discussed later. The shoulder at 1380 cm$^{-1}$ represents B–O–B moieties$^{93}$.

Referring to the IR spectra of PBSs obtained by Zinchenko et. al.$^{82}$, the B–O–B related shoulder is much weaker in our case. We think this difference is most probably due to our above-mentioned refinement procedures. Nevertheless, B–O–B bonding can still exist in rPBSs, due to reversible condensation reactions among borono ends. Severe dehydration might in principle transform the supramolecular elastomer into a covalently cross-linked rubber. Peaks located at 1150 cm$^{-1}$ (Fig. 2.5 (a)) and 3180 cm$^{-1}$ (Fig. 2.5 (b)) correspond to B–O–H bending of a mixture of trigonal and tetrahedral boron$^{88}$, and the bound B–O–H moieties$^{82}$, respectively. Their absence indicates that we have removed the BA to a large extent. The appearance of a tiny peak in the spectrum of rPBS1 at 3180 cm$^{-1}$ indicates that rPBS1 was not completely refined. As samples were dried in a vacuum oven before measurements, the amount of B–O–B moieties has increased accordingly because of the unexpected condensation reactions. This also explains the absence of peaks at 3180 cm$^{-1}$ and 3600 cm$^{-1}$ in Fig. 2.5 (b), which are assigned to the H-bonded B–O–H groups and free B–O–H groups$^{82,83}$.
Figure 2.5: FTIR spectra of rPBSs measured at room temperature under the ATR mode.

One remarkable but rarely reported band appears in both the spectra of PBSs and BA around 890 cm$^{-1}$, but is absent in the spectrum of pristine PDMS. This band is associated with the out-of-plane bending of B–O–H groups$^{88,94}$. This provides further evidence that PDMS has indeed been modified.
2.3.3 The molecular weight distribution and its evolution during the modification reaction

![Graph showing molecular weight distribution and its evolution during the modification reaction.](image)

**Figure 2.6:** Conventional calibration curve of PDMS standards measured at 40 °C in THF (a). GPC results of pristine PDMS, PBSs modified for 1 and 6 hours (b).
Figure 2.6 (a) shows a conventional Gel Permeation Chromatography (GPC) calibration curve of PDMS standards in THF at 40 °C. The relation between the molar mass of the polymer $M$ and the retention time $t$ can be described by a Mark-Houwink equation, Eq. 2.1.

$$\log t = \log k + \alpha \log M.$$  \hspace{1cm} (2.1)

$k$ and $\alpha$ are determined as 16.67 and -0.07, by linear fitting the plot in Fig. 2.6 (a). Based on this correlation of molar mass versus retention time, we are able to obtain the molar mass distributions (MDs) of the commercial PDMSs and synthesized PBSs. The GPC chromatograms of PBS samples, which have reacted for 1 and 6 hours, as well as the pristine PDMS, are shown in Fig. 2.6 (b). Clearly, MDs shift towards lower $M$ as the reaction proceeds. From such MDs, the number and weight average molecular masses ($M_n$ and $M_w$, respectively) can be directly calculated according to the expressions, Eq. 2.2 and Eq. 2.3

$$M_n = \frac{\Sigma_i M_i n_i}{\Sigma_i n_i},$$  \hspace{1cm} (2.2)

$$M_w = \frac{\Sigma_i M_i^2 n_i}{\Sigma_i M_i n_i},$$  \hspace{1cm} (2.3)

where $n_i$ is the number of chains of degree of polymerization, $i$, and $M_i$ represents the molar mass of one such chain. The peaks at longer retention time, beyond 10 minutes, are caused by injection pressure, which is an unavoidable effect of sample injection.

In order to correct for the overlapping injection peak, GPC data were numerically fitted by a linear combination of gaussian curves. The MD is obtained by subtracting the injection peaks as shown in Fig. 2.7 (a). The ‘intensity’ is proportional to the total number of segments at a particular $M_i$, $I \propto n_i M_i$. Corrected MDs of all rPBS samples are given in Fig. 2.7 (b), based on which $M_n$ and $M_w$ of all rPBSs are calculated. The results are summarized in table. 2.1.
Figure 2.7: Fitting curve of PBS reacted for 6 hours (a). MMD of PBSs reacted up to 6 hours (b).
Table 2.1: Summary of $M_n$, $M_w$ and $k_h$ of each intermediate steps. $k_{hn}$ and $k_{hw}$ were calculated from the $1/N_n(t) - 1/N_n(0)$ and $1/N_w(t) - 1/N_w(0)$ curves, respectively.

![Figure 2.8: 1/N_n(t) - 1/N_n(0) and 1/N_w(t) - 1/N_w(0), as well as the absorbance of Si–O–B moieties are plotted versus time.](image)

The evolution of $M_n$ and $M_w$ as a function of reaction time are then used to reveal the kinetics of the synthetic reaction of PBSs, by plotting $1/N_n(t) - 1/N_n(0)$ and $1/N_w(t) - 1/N_w(0)$ versus reaction time (Fig. 2.8). $N_n(t)$ and $N_w(t)$ represent the number average and weight average degree of polymerization of the PBS products, and $N_n(0)$ and $N_w(0)$ belong to the raw PDMS. The relation between molar mass and degree of polymerization ($N$) is described as $N_n = M_n/m$ or $N_w = M_w/m$, where $m$ is the
molar mass of the repeating unit of polymer (−OSi(CH₃)₂− in this dissertation). In Fig. 2.8, the increasing trend in the y-axis reflects a decreasing average molar masses. Within experimental accuracy, the \( N_w \) is twice \( N_n \), which is an indication that molecular cleavage occurs as a random scission process.

Referring to the Ekenstam relationship\(^96\), based on random scission of the chains, the reaction rate constant \( k_h \) can be determined from the slopes of the plots, as

\[
\frac{1}{N_w(t)} - \frac{1}{N_w(0)} = \frac{1}{2}k_ht, \tag{2.4}
\]

\[
\frac{1}{N_n(t)} - \frac{1}{N_n(0)} = k_ht. \tag{2.5}
\]

If the molecules undergo random scission, the MD tends towards a Kuhn distribution, and the slope of \( 1/N_n(t) - 1/N_n(0) \) vs. time (Eq. 2.5) should be twice as big as that of \( 1/N_w(t) - 1/N_w(0) \) vs. time (Eq. 2.4). The factor 2 originates from the ratio \( M_w/M_n = 2 \), which is characteristic of a Kuhn shape MD resulting from random scission\(^97\). Obviously the factor 1/2 in Eq. 2.4 is a direct consequence. The leveling off of the curves in Fig. 2.8 indicates that \( k_h \) of our reaction decreases with time. Since we have, for all PBSs, collected un-reacted boric acid in the purifying step, we are sure that the decrease of \( k_h \) is not caused by depletion of BA, but by the rising viscosity due to the modification itself. We infer that the synthesis of PBSs follows a diffusion limited reaction. We noticed that both the \( 1/N_n(t) - 1/N_n(0) \) and \( 1/N_w(t) - 1/N_w(0) \) relations can be described with an exponential grow function, Eq. 2.6, with reasonable precision.

\[
y = A(1 - \exp(-t/B)). \tag{2.6}
\]

\( A \) and \( B \) values of each fitting curve are included in Fig. 2.8. The \( B \) value reflects the characteristic time in which the reaction rate slows down. The ratio of two \( A \) values (\( A \) of red curve : \( A \) of black curve \( \approx 2 \)) also confirms a random scission process. Therefore we were able to determine the variation of \( k_h \) with time,

\[
k_h = \frac{A}{B} \exp(-t/B) \tag{2.7}
\]

from the derivatives of Eq. 2.6.
Additionally, the absorbance of Si–O–B moieties as a function of reaction time was collected from the normalized IR spectra in Fig. 2.5, and displayed together with the \(1/N_n\) and \(1/N_w\) curves in Fig. 2.8. The Si–O–B absorbance exhibits the same trend as the \(1/N_n\) and \(1/N_w\) curves, which are based on GPC analysis. It demonstrates an increasing number of Si–O–B moieties as the reaction proceeds. This confirms further that new chain ends formed upon scission are modified by borono groups, because the number of chain ends is proportional to \(1/N_n\).

### 2.3.4 Development of mechanical properties upon modification

The influence of BA modification on the viscoelastic properties of PDMS is revealed by rheometry. Figure 2.9 shows a dramatic increase in the magnitude of the dynamic storage \(G'\) and loss \(G''\) moduli upon modification. The angular frequency, where \(G'\) and \(G''\) intersect, is equal to the inverse of terminal relaxation time, \(\tau\), of the system. The increasing number of reversible cross-links leads to not only a much stiffer material, but also a decreased molecular mobility. Therefore, \(\tau\) is increased. To confirm the formation of boroxane structure upon dehydration, we placed rPBS6 under 100 mbar and 200 °C for 1 hour in a vacuum oven. Rheology confirms the formation of boroxane structures via the appearance of an additional \(G''\) peak. We propose that the extra \(G''\) peak is indicating that the flexible short molecules start to locally form branched networks via the mild dehydration, giving rise to an additional time scale\(^{98}\).

Figure 2.10 shows the tensile dynamic moduli of rPBS6 sample as a function of temperature. The peak of the loss modulus and the steep decrease of the storage modulus at about -100 °C, indicates that the glass transition temperature \(T_g\) of rPBS6 has significantly increased compared to pristine PDMS (-120 to - 150 °C). This confirms that boric acid modification does enhance the interaction among the PBS molecules. The noisy signal above \(T_g\) is due to indentation of the DMA probe. Below \(T_g\), the storage modulus of about 3 GPa is similar to that of common engineering plastics, such as polypropylene\(^{99}\), polylactic acid\(^{100}\), poly(methyl methacrylate)\(^{101}\), etc.
Figure 2.9: Dynamic storage ($G'$) and loss ($G''$) moduli of PBSs of different reaction time, measured at 20 °C.

Figure 2.10: Tensile dynamic moduli of rPBS6. Heating at 5 °C/min and oscillating at 1 Hz.
2.4 Conclusions

The modification of polydimethylsiloxane (PDMS) with boric acid (BA), in order to produce polyborosiloxanes (PBSs), constitutes a random scission process resulting in a Kuhn distribution of chain lengths. While PDMS chains are cut, the new chain ends get modified by polar, hydrogen-bonding moieties, formed out of boric acid. These end groups are initially heterogeneous, with some 'polymerized' boric-acid owing to B−O−B binding. As evidenced by IR spectroscopy, these groups contain both 'boranol' (B−O−H), and 'boroxane' (B−O−B) moieties. These heterogeneous end groups can be converted into Si−O−B(OH)$_2$ moieties by letting them hydrolyze at room temperature at ambient humidity. Boric acid released by this reaction can be removed easily by filtration. Although the mean chain length of the polymer decreases upon the modification, rPBSs are mechanically stiffened owing to the strong (hydrogen-bonding) interactions between the modified chain ends. So this material may be denoted a supramolecular elastomer. However, upon severe dehydration the boranol groups of the chain ends condense into boroxane linkages. As exposure to ambient humidity at room temperature, the boroxane linkages hydrolyze and the material returns to be a supramolecular elastomer.
The multifarious reversible cross-links in polyborosiloxane

This chapter is for a large part based on:
3.1 Introduction

During the last decade, there has been growing interest for self-healing materials (SHMs). The scope of SHMs covers polymers, metals, concretes, ceramics, and composite materials. One of the definite definitions of self-healing is, the ability to repair damage and restore the lost or degraded properties or performance using resources inherently available to the system\textsuperscript{2}. Currently, the most commonly used terms for categorizing SHMs are the "extrinsic" and "intrinsic" systems. In the extrinsic category, self-healing relies on the usage of added healing-agents, such as solvents, adhesives, catalysts, bacteria, etc\textsuperscript{2,4,5,6,7,8,9,10}. In contrast, their counterpart "intrinsic" SHMs self-heal due to the reversible cross-links between the constituent molecules themselves\textsuperscript{2,11}.

Polyborosiloxanes (PBSs) were invented during the Second World War with the intention of solving the shortage of natural rubber. However, they were found to be viscoelastic fluids\textsuperscript{41}, instead of rubbery solids. They have been used for several applications using names, such as Silly Putty, bouncing putty\textsuperscript{74}, dilatant compounds\textsuperscript{76}, etc. It is well accepted that the pronounced increase of mechanical moduli upon modification of polydimethylsiloxane (PDMS) by boric acid (BA) is due to hydrogen–bonds (HBs) between BA based moieties of the PBS. As these HBs are reversible and are readily re-established after breaking, PBS has intrinsic self-healing capabilities. Thus, both microscopic cracks and macroscopic failures of PBSs heal without external stimuli.

The aim of this study is to provide an understanding on the physics and chemistry behind the self-healing behavior of PBS. We will demonstrate that PBS molecules not only interact via the well-understood HBs, but also through other interactions.

3.2 Experimental section

3.2.1 Materials

PBS was synthesized from poly(dimethylsiloxane) (PDMS) and boric acid according to methods described in our earlier publication\textsuperscript{41}. In this chapter we used refined PBS
(rPBS) with a number average molar mass \(M_n\) of about 3720 g/mol. In this rPBS, the BA modified chain ends are predominantly borono moieties, \(-O-B(OH)_2\), as the excessive BA that polymerized during synthesis has been hydrolyzed and removed. Trimethylsiloxy terminated PDMS with a similar \(M_n\) of 3780 g/mol (ABCr Gmbh & Co.KG, Karlsruhe, Germany.) was purchased and used as a reference. Cyclohexane of reagent plus grade (Sigma–Aldrich) served as solvent in the refining step.

### 3.2.2 Methods

In Chapter 2, we discussed the formation of the unexpected boroxane along synthesis, during which boric acid polymerized with borono moieties. Such boroxane structure can be easily hydrolyzed in the presence of moisture. Based on such understanding, Refinement of PBSs was carried out in a modified, more efficient way, as compared to the method introduced previously. We added a few droplets of demineralized water into the PBS/cyclohexane solution, and stirred the mixture at the maximal speed (1200 rpm) on a magnetic stirrer at room temperature for 1 minute. The added water enhances the hydrolysis of the boroxane moieties, \(B-O-B\), and renders refined PBS molecules and a boric acid precipitate. We filtrated the boric acid precipitate and repeated such stirring/filtering cycles in the presence of water. After 6 cycles, we no longer observed boric acid precipitation, and harvested crystal-clear and transparent PBS elastomer upon evaporation of cyclohexane. As compared to the former refining method, this modified one took only 1 hour to complete the entire refinement. The hence produced refined PBS will be referred to as ‘rPBS’. Before investigation, a rPBS sample was conditioned under ambient atmosphere in order to hydrolyze the chemical cross-links between PBS molecules. Dehydrated rPBS was produced by storing rPBS under 100 mbar and 150 °C in a vacuum oven until the weight no longer decreased.

Figure 3.1 shows an unrefined PBS sample, which contains BA contamination. The excessive BA cross-linked with PBS molecules during IPA removal, which results in a clear appearance in Fig. 3.1a. Such BA-PBS cross-links can be rapidly hydrolyzed by water from ambient environment, and recover BA particles. Therefore the sample becomes turbid after about 1.5 h (Fig. 3.1b). Figure 3.1c shows a clear
PBS, which was obtained by dehydrating the turbid PBS sample at 150 °C and 100 mbar for about 2 h.

Figure 3.1: Graphic demonstration of the un-refined PBS that has been, a. dehydrated, b. hydrolyzed under ambient humidity, and c. dehydrated again.

Fourier transform infrared (FTIR) spectroscopy was performed with a Perkin–Elmer Spectrum 100 series FTIR spectrometer, using the attenuated total reflectance (ATR) mode. Rheologic measurements were carried out on a TA AR G2 Rheometer, using plate–plate geometries: an upper plate of diameter of 40 mm was used for pristine PDMS, and a 8 mm plate for the viscoelastic rPBSs. Solid state magic angel spinning (MAS) $^{11}$B NMR was preformed on a Bruker Avance 400 spectrometer operating at 128.3 MHz. Samples were prepared in 4 mm zirconia rotors, rotated at 11 kHz. Typically, 2000 scans were collected at a spectral width of 25 kHz and an acquisition time of 5 ms. The spectra were referred to a 0.1 M aqueous solution of H$_3$BO$_3$, used as an external standard set to 0 ppm.

3.3 Results and discussion

As compared to our earlier refining procedure, the modified procedure takes only 1 hour rather than several weeks. The modified refining procedure is more efficient in hydrolyzing the polymerized boroxane moieties, which were formed during synthesis. In the former case, we let water molecules in the air penetrate into the PBS/cyclohexane solution and hydrolyze the boroxane moieties. However, in this chapter, we directly add water and disperse it by violent stirring. The increasing concentration and total surface area of water thus accelerate the refinement. Therefore, we harvest PBS molecules of well-defined structures (Fig. 3.2).
The multifarious reversible cross-links in polyborosiloxane

Figure 3.2: Molecular structures of the rPBSs. The methyl groups on Si are not drawn explicitly.

Figure 3.2 represents the molecular structure of rPBSs. A small fraction of PBS molecules bear only one borono group, \( -\text{O} - \text{B(OH)}_2 \). This is due to the fact that PBS was synthesized by cleaving and modifying PDMS of high molar mass in the presence of boric acid. Only the 'new' chain ends formed upon cleaving are modified by borono moieties. The number averages of \( a \) and \( b \) are about 49, as determined by gel permeation chromatography. The limited chain length, low glass transition temperature (\( \sim 90 \, ^\circ \text{C} \)), and the borono moieties together make PBS a supramolecular elastomer. Boron atoms in \( -\text{O} - \text{B(OH)}_2 \) possess a \( sp^2 \) hybridized trigonal configuration, which encourages them to accept lone-pair electrons by the vacant \( p \)-orbital to reach their octet. Therefore, a trigonal boron atom can dynamically transform into a \( sp^3 \) hybridized tetrahedral boron, by forming a boron–oxygen bond with the hydroxyl group of a neighbor molecule. The formation of such boron–oxygen bond may also be referred to as the Lewis base–Lewis acid interaction. In Figure 3.3 we sketch three possible connections of PBS molecules under ambient conditions as (a) H–bonding, (b) reversible trigonal to tetrahedral boron transformation, and (c) dynamic formation of boroxine. Figure 3.3 (a) only represents the H-bonded molecules in a 2D plane, but in fact the H-bonded molecules are 3D configured.

As the borono groups of rPBS resemble organo-boronic acid, which spontaneously forms an entropically favored reversible trimeric boronic anhydride, we suggest the borono moieties also form reversible trimeric rings under ambient conditions (Figure 3.3, (c)). Such cyclotrimeric anhydride of boric acid is denoted 'boroxine' or 'boroxol ring', while other dehydrates are generally named 'boroxane'.
Figure 3.3: Interactions between −O−B(OH)$_2$ moieties at ambient conditions. (a) Dashed lines represent the HBs$^{92}$. (b) Formation of a tetrahedral configured boron atom. (c) Formation of boroxine, a trimeric ring of borono groups connected by boroxane bonds (B−O−B). Each unsaturated oxygen in the sketches connects with a Si atom of the PBS backbone.

In the FTIR spectra of rPBS (Figure 3.4a), the band at 890 cm$^{-1}$ can be assigned to vibration of hydroxy groups connecting with both $sp^2$ and $sp^3$ boron atoms$^{105}$. The peak centered at 1340 cm$^{-1}$ and the shoulder at 1380 cm$^{-1}$ correspond to the Si−O−B and B−O−B moieties$^{93}$, respectively. The shrinking of the band at 890 cm$^{-1}$ and the growth of the peak at 1380 cm$^{-1}$ upon dehydration constitute solid evidence of the structural changes, where the amount of B−O−B moieties increases at a cost of hydroxyls.

Figure 3.4b shows the $^{11}$B solid state MAS NMR spectra of both a conditioned and a severely dehydrated rPBS samples. The conditioned rPBS shows a peak at -2 ppm and a shoulder at -4 ppm in its NMR spectrum. However, in the spectrum of the severely dehydrated rPBS, there is only one broad singlet centered at -4 ppm. Regarding the chemical structure of rPBS before and after dehydration, we suggest
The multifarious reversible cross-links in polyborosiloxane

Figure 3.4: FTIR spectra of pristine PDMS and rPBS samples (a). $^{11}$B solid state MAS NMR spectra of rPBS samples that were stored prior to the measurements under ambient atmosphere (black curve) and in a vacuum oven at 150 °C and 100 mbar (red curve) (b).

that the two peaks centered at -2 ppm and -4 ppm correspond to the individual borono moieties and to the condensed structures (B−O−B), respectively. Such interpretation
is applicable to the spectrum of the severely dehydrated rPBS, where the polymerization of borono groups leads to the disappearance of peak at -2 ppm and a predominant singlet at -4 ppm in the NMR spectrum.

Djanashvili et al.\textsuperscript{106} have extensively discussed the resonance of trigonal boron and tetrahedral boron. They suggest that if boron atoms in an analyte are all trigonal configured, it shows a sharp peak at 20 ppm in the $^{11}$B NMR spectrum. Transition of boron atoms from trigonal to tetrahedral configuration leads to a chemical shift up-field (to the right) and broadens the peak, because the tetrahedral borons suffer more from quadrupolar interaction. As the fraction of tetrahedral configured boron reaches 1, the chemical shift stops moving at -20 ppm.

In Fig. 3.4b, the observed spectral changes upon dehydration of rPBS hence indicate that oxygen atoms from borono groups bridge between boron atoms.\textsuperscript{107} This leads to an increasing number of boroxane moieties. Meanwhile, the fraction of tetrahedral configured boron increases. Although, the resonance at $\delta=-4$ ppm appears in both spectra, the difference in broadness suggests different boroxane structures. In conditioned rPBS, the reversible chemical cross-links are mainly trimeric boroxines. In the severely dehydrated material, most of the borono groups polymerize and result in boroxane. The boroxane structure exhibits much more variation than the well defined boroxine moieties. The number of borono groups that participate in forming each boroxane joint may differ, as well as the spatial configuration. For instance, boroxine is a specific boroxane joint, which comes from the polymerization of 3 borono groups. However, a general boroxane joint can also be made of 2 borono groups or an even larger number. Thus, the dehydrated structure that involves boroxanes exhibits a much broader peak than the boroxine dominant non-dehydrated structure.

We propose an example of a boroxane connected moiety in severely dehydrated rPBS in Figure 3.5. This moiety consists of two $sp^2$ borons and two $sp^3$ borons, which may either be turned from four borono groups, or by attaching one borono group to an existing boroxine. We use the 3D representation of this moiety (Fig. 3.5b) to emphasize that PBS molecules upon dehydration form 3D cross-links.
The multifarious reversible cross-links in polyborosiloxane

Figure 3.5: Schematic representation of a boroxane connected moiety, given in 2D (a) and 3D (b). Boron and oxygen are given as yellow and red balls, respectively.

Figure 3.6: Rheology of rPBS and PDMS of equivalent molar mass. Black, red and blue colors correspond to pristine PDMS ($M_w \approx 3780$), rPBS ($M_w \approx 3720$) and the severely dehydrated rPBS. □ and ○ represent experimental storage and loss moduli. Solid and dashed lines represent the modeled curves based on the Maxwell model given as the inset.

The multifarious dynamic cross-links within the rPBS material tremendously affect the mechanical performance. As seen in Figure 3.6, the pristine PDMS and rPBS of similar molar mass have very different mechanical properties. Within the experimental frequency window, both compounds behave as Maxwell fluids. The
terminal relaxation time is defined as \( \tau = \eta / G_0 \), where \( G_0 \) and \( \eta \) refer to the plateau modulus and zero shear viscosity of the system. \( \tau \) equals the inverse of the angular frequency, at which the storage and loss modulus curves intersect. \( G_0 \) represents the high frequency plateau of the elastic modulus. This is related to the density of dynamic cross links, similarly to how the modulus of a rubber is related to the cross-link density \(^{109}\).

Pristine PDMS with the moderate molar mass as examined here relaxes rapidly due to the weak intermolecular interactions. Therefore it is a thin fluid. The reversible cross-links in rPBS lead to the increased elastic modulus, as well as the increased \( \tau \), comparing to the pristine PDMS. The severely dehydrated rPBS behaves differently, as it shows two distinct maxima in the loss modulus curve, which indicate two relaxation processes.

The critical entanglement molar mass of PDMS was determined as 12,000 g/mol \(^{110}\), so we attribute the fast relaxation of pristine PDMS to a combination of diffusion and reptation of molecules \(^{111,112}\). However, the relaxation time of rPBS may already be an overall effect of reptation (\( \tau_{rep} \)) and dynamic chain life (\( \tau_{dyn} \)) \(^{111,113}\). To interpret the two loss peaks of the dehydrated rPBS, we have to take the covalently cross-linked structure into account. Mcleish et al. \(^{114,115}\) have investigated the rheology of the H-shaped branched polymers. They have linked the slow relaxation time to reptation. The faster relaxation process is due to the relaxation of the "arms", which is caused by the retraction of chain stretch. Our covalently cross-linked rPBS is in fact a branched polymer, and therefore shows two distinct loss peaks. Nevertheless, dehydration only converts the nature of cross-links without altering the total cross-link density, so that rPBS and its dehydrated counterpart possess the same plateau modulus.

The dynamic supramolecular network of rPBS can be easily transformed into a covalent network, and vice versa. rPBS that has undergone repeated dehydration and hydrolysis does not exhibit significant change in appearance or mechanical performances. This feature broadens the applicability, as rPBS can provide a reasonable stiffness and toughness over a wide frequency range in the dehydrated form. At humid conditions, water molecules hydrolyze the covalent network, thus recover a
living elastomer.

Figure 3.7: Graphic demonstration of the self-healing properties of rPBS.

Figure 3.7 demonstrates the self-healing process of rPBS. Figure 3.7a shows a crystal-clear and colorless pine tree that made of rPBS. We cut this pine tree shaped rPBS into three pieces (Fig. 3.7b). We carried out the self-healing experiment by reconnecting these three pieces, without compression yet in a mould. Figure 3.7c shows a scarless pine tree, which was obtained upon 3 h self-healing. The edge of the self-healed pine tree (Fig. 3.7c) becomes less sharp as compared to the initial one in Fig. 3.7a. This can be attributed to the mobility of PBS molecules, which is essential for the self-healing process of rPBS.

3.4 Conclusions

The properties of refined polyborosiloxane (rPBS) are governed by multifarious cross-linking mechanisms. Under ambient conditions, reversible boroxine moieties accompany other dynamic intermolecular interactions, such as H-bonds and Lewis base – Lewis acid interactions. These dynamic cross-links not only establish a supramolecular structure, but also mechanically enhance rPBS. Upon severe dehydration, the cross-links become covalent, where boroxane moieties replace most of the boroxine and physical cross-links. Such a change has been confirmed by $^{11}$B solid state MAS NMR, rheology and FTIR techniques.
Self-healing nanocomposites. A interpenetrated molecule-filler network leads to a separation of time-scale
4.1 Introduction

One approach towards self-healing materials is to bestow soft non-glassy polymers with reversible cross links, leading to what may be denoted a supramolecular elastomer. The dynamic nature on the molecular level enables such materials to heal spontaneously after fracturing, as reversible bonds can form again after being broken. In principle breaking and reformation of bonds can be repeated indefinitely. In fact due to thermal agitation, the reversible bonds are being formed and broken continuously, while a stable equilibrium number density of bonds is maintained. This class of self-healing materials is denoted intrinsically self-healing, to distinguish them from materials in which self-healing properties are owing to inclusions filled with healing agents, which are released upon fracture and consumed while healing a crack.

Unfortunately, the concept of intrinsically self-healing materials has an intrinsic drawback. The very same dynamic nature of the cross links which enables self-healing, also allows the material to flow. These materials are intrinsically visco-elastic fluids, although the terminal relaxation time and viscosity may be relatively large. The elastic part of their frequency-dependent modulus $G'(\omega)$ approaches to 0 as the frequency $\omega$ goes to 0. Obviously, this is undesirable for a structural material, as it will inevitably deform gradually under a sustained load, even under the load of gravity.

At first sight this problem seems to be insoluble. Diminishing the dynamic nature of the cross links in order to slow down deformation under load, will at the same time deteriorate the self-healing capabilities of the material. For instance, quite a few ureidopyrimidinone (UPy) based self-healing polymers resist the gravity due to the highly self-organized hydrogen-bonding pairs, however, the contact time required for self-healing is normally from $10^2$ s onward.

Our solution to this dilemma is to achieve a 'separation of time-scales’. The relatively fast dynamics, associated with the terminal relaxation time of the supramolecular elastomer, which enables recovery of the cross links after fracture, should be preserved. At the same time the dynamic elastic modulus at low frequencies (long time scales), where it vanishes for a supramolecular elastomer, should be boosted. In
this chapter, we demonstrate how this can be realized by combining a supramolecular elastomer matrix with a self-organized skeleton consisting of hard nanofiller particles.

4.2 Experimental

4.2.1 Chemicals

Trimethylsiloxy terminated linear polydimethylsiloxanes (PDMSs) in viscosity grades of 100 cSt (ABCr GmbH & Co.KG, Karlsruhe, Germany.) was used as a reference material in rheology. The organo-modified nano clay (OMNC) used in this chapter is a commercial thixotropic additive under trade name, Cloisite 20 (Rockwood Additives). Natural montmorillonite particle has been purchased under trade name Nanofil 116 and used for comparison. Isopropyl alcohol (IPA) was purchased from Fisher Scientific to mix the OMNC with PBS. The self-healing matrix used in this chapter is rPBS6 as referred to Table 2.1 in Chapter 2.

4.2.2 Sampling

rPBS6 and filler particles were weighed and directly mixed at the target filler concentrations in beakers. IPA was then supplied to immerse these two chemicals. As IPA can efficiently dissociate the reversible cross links of PBS, PBS/IPA solutions with precipitated particles were obtained within half an hour. The mixtures were mixed and heated with magnetic heating plates, until most of IPA vanished. All composites were processed with a twin-screw rubber mill at room temperature for 5 minutes to improve the homogeneity. In order to hydrolyze the unexpectedly formed boroxane moieties during solvent evaporation, all samples were compressed into thin film of several folds of microns and conditioned for 1 week under ambient humidity. The conditioned samples were again processed with the rubber mill to produce thick films (~1 mm) and thin films (~50 µm) for rheology and XRD measurements, respectively. PDMS of 100cSt was mixed with OMNC particles to produce reference nanocomposites, however, OMNC particles started precipitating as soon as stopped stirring, even at filler concentration of 40%.
4.2.3 Characterization

A Bruker-AXS D8 Discover X-ray diffractometer was used to examine the morphology and dispersion of the particles in the PBS matrix. Cross-coupled Göbel mirrors were used to filter the CuKα radiation (λ = 0.154 nm), and we used a Hi-Star 2D detector.

Rheologic measurements were carried out on a TA AR G2 Rheometer, using the plate-plate geometry: an upper plate of diameter of 40 mm for pristine Polydimethylsiloxane (PDMS), and a 8 mm plate for the PBSs, because of their much larger stiffness.

4.3 Results and Discussion

Physically, PBS behaves as an almost perfect Maxwell fluid. The dynamic storage and loss moduli are fitted well by the Maxwell expressions

\[
G'(\omega) = \frac{G_1 \eta^2 \omega^2}{\eta^2 \omega^2 + G_1^2}, \quad G''(\omega) = \frac{G_1^2 \eta \omega}{\eta^2 \omega^2 + G_1^2} \tag{4.1}
\]

(see Fig. 4.1), even up to angular frequencies that are an order of magnitude larger than the inverse of the terminal relaxation time \(\tau_1\). In Eq. 4.1, \(\omega\) is the angular frequency of the oscillatory shear stress and shear strain, \(\eta\) is the zero-shear viscosity, and \(G_1\) is the high-frequency plateau modulus. The characteristic time (terminal relaxation time) is \(\tau_1 = \eta/G_1\). At \(\omega = 1/\tau_1\), \(G''(\omega)\) is a maximum, and the predominantly elastic high-frequency behavior crosses over to predominantly viscous low-frequency behavior, as \(G''(\omega)\) crosses \(G'(\omega)\).

More importantly, random scission process endows PBS a poly-dispersity of 2, such feature ought to broaden the loss modulus curve. However, one Maxwell unit in our case is already capable of describing the dynamic rheology of PBS in a largely accurate manner. Therefore, it again proves the supramolecular nature of PBS, which dynamically assemble towards a macromolecular structure, and eventually approaches to an equilibrium number density of cross-links.
Figure 4.1: Rheological properties of PDMS and rPBS of similar molar mass ($M_n \approx 2200$). □ and ○ represent experimentally measured storage and loss modulus. Solid and dashed lines are the fitting curves based on the Maxwell model.

Unmodified PDMS of about the same average molar mass seems to behave as a Maxwell fluid (Fig. 4.1), although its terminal relaxation time and high-frequency plateau modulus are about two orders and five orders of magnitude smaller than for rPBS. Due to experimental limitations we cannot establish if this Maxwell behaviour holds for angular frequencies beyond it’s $1/\tau_1$ value (or even completely up to it). Clearly, the effect of the borono end groups on the mechanical properties is huge, but it still does not change the gravity driven fluidic feature of rPBS.

To overcome this problem and aim at developing the engineeringly applicable self-healing nanocomposites, which is significantly robust and rapidly recovering, we have designed an interpenetrated filler/polymer network. We establish a hard skeleton by means of incorporating 2D nano-sized platelets, which interpenetrates throughout the dynamic network of PBS molecules. Thus, the stationary skeleton and dynamic rPBS phase respectively govern the free-standing (or load-bearing) and self-healing functionalities.
We selected organically modified nanoclay (OMNC) platelets as the building units of the skeleton. OMNC consists of montmorillonite (MMT) platelets and surface modifiers, which are mostly dioctadecyl(dimethyl)ammonium (C18) molecules. Thus, OMNC has a low surface hydrophilicity. We propose the reduced interaction between OMNC platelets and the hydrophilic borono groups of PBS molecules will not increase the time of self-healing ($\tau_1$). Figure 4.2 represents the interpenetrated network schematically. Stacks made of a number of OMNC platelets construct a porous skeleton, in which PBS molecules penetrate and build another network.

Figure 4.2: Schematic representation of the interpenetrated network within the self-healing nanocomposite. Red spots highlight the intermolecular interaction of PBS molecules.

Our concept on combining rPBS with OMNC is proved valid by comparing the rheological properties of the rPBS nanocomposites in Fig. 4.3. The self-healing characteristic, $\tau_1$, of the OMNC/rPBS nanocomposite is identical to that of rPBS. However, as MMT platelets are used $\tau_1$ becomes 10 times bigger. This is due to the particle/molecule interaction, which replaces a fraction of intermolecular network with particle/molecule network. As a result, the mobility of PBS molecules are decreased, thus a longer self-healing characteristic. Meanwhile, such particle/molecule interaction does not mechanically enhance the nanocomposite either.
Figure 4.3: Rheological properties of rPBS nanocomposites, in which the filler mass fraction in each nanocomposite is 0.1.

Figure 4.4: Rheology of the OMNC/rPBS nanocomposites.
Figure 4.4 shows the rheological results of the OMNC/rPBS nanocomposites up to an incredibly high filler loading. Upon increasing the filler content, both storage and loss moduli are dramatically reinforced, accompanied with the broadening of the loss curve. As filler mass fraction is as high as 0.7, the nanocomposite resembles rubber within the operation window of the rheometer, which is no longer mechanically frequency dependent. As expected, relaxation time, $\tau_1 \approx 1.26$ s that inversely equals to the maximum of loss curve does not deviate much from that of rPBS (0.9 s). The broadening of loss curves suggests that OMNC particles have induced additional relaxation processes, which alters rPBS from a visco-elastic fluid to a free-standing solid. Such alteration can be noticed from the storage modulus of the OMNC/rPBS nanocomposites at the lowest programmable frequency (modulus at 0.01 rad/s is abbreviated as $G_{0.01}$), which increases as a function of filler content. If we assume $G_{0.01}$ as the elasticity of the non-destructive filler-skeleton and represent the mechanical contribution of such skeleton as a second spring connecting in parallel to the Maxwell arm, we can interpret the rheological results with the standard linear solid (SLS) model\textsuperscript{57,59}, Eq. 4.2. The fitting results will be discuss later in Fig. 4.6.

$$G'(\omega) = \frac{G_{0.01}(1 + \tau_1\tau_\sigma\omega^2)}{1 + (\tau_1\omega)^2}, G''(\omega) = \frac{G_{0.01}(\tau_\sigma - \tau_1)\omega}{1 + (\tau_1\omega)^2}, \tau_\sigma = \frac{\eta_1(G_1 + G_{0.01})}{G_1G_{0.01}}. \quad (4.2)$$

Due to the limited frequency window of the rheometer, it might be risky to conclude that the OMNC/rPBS nanocomposites stay solid, for instance using the SLS model, in longer time scales. Therefore, we turn to creep experiment as an alternative approach of the oscillatory one. Creep experiment can last up to 99 hours, which helps us reveal the long term behavior of nanocomposites in more details. Figure 4.5 shows the compliance curves as a function of time, which reach equilibrium at large time scale. Fitting the creep curves at large time scale allow us to collect additional parameters. $a$ and $b$ of the linear fitting function are inversely equal to the viscosity ($\eta_{creep}$) and plateau modulus ($G_{creep}$) of one of the filler-induced relaxation processes at large time scale. Together with $\tau_1$ and $G_1$, we have parameters of two relaxation processes, located respectively at long time limit and high frequency limit. We attempt to describe the rheological behavior of the nanocomposites by applying the simple Maxwell model twice in Fig. 4.6.
Figure 4.5: Creep results of the OMNC/rPBS nanocomposites. ○ and □ represent filler mass fraction of 0.1 and 0.4, respectively. Solid lines are the linear fitting to the creep curves at large time scale.

Figure 4.6 shows the frequency dependent rheological properties of nanocomposites at mass fractions of 0.1 and 0.4, as well as the fitting curves based on SLS and Maxwell models. We notice that at low filler content we can not precisely predict the long term performance of the nanocomposites by SLS model, because $G_{0.01}$ overestimates the elasticity of the nanocomposite at large time scale ($G_{creep}$) for nearly 7 folds. However, such overestimation is rapidly reduced to 1.6 times when mass fraction of filler reaches 0.4. The red curves are based on using the Maxwell model twice respectively at the long time limit and high frequency limit of the rheological measurements. It predicts the long time scale mechanical performance of the OMNC/rPBS nanocomposites in a more reliable way than the SLS model.

We have plotted $G_1$, $G_{0.01}$ and $G_{creep}$ of all OMNC/rPBS nanocomposites as a function of filler content in Fig. 4.7. Clearly, as filler mass fraction exceeds 0.1, the modulus vs. filler mass fraction plot follows a polymer law, $G = A\phi^\alpha$. (more input)

Figure. 4.8 summarises the WAXD spectra of the OMNC/rPBS nanocomposites at a
Figure 4.6: Fitting curves of the oscillatory results of the OMNC/rPBS nanocomposites with simple mechanical models. Black curves are based on the SLS model, red curves are produced by utilizing the Maxwell model twice.

Few specific concentrations. The X-ray reflection at $2\theta = 12^\circ$ is caused by the PBS matrix. X-ray reflection located at $2\theta = 3^\circ$ and $1.3^\circ$ represent the interlayer spacings.
**Figure 4.7:** A summary of the plateau moduli obtained from oscillatory and creep measurements.

\[ G_{\text{high}} = G_1 + G_2 \]
\[ G = A\phi^\alpha \]
\[ \alpha_{\text{creep}} = 4.5 \]
\[ \alpha_2 = 3.7 \]
\[ \alpha_{\text{high}} = 2.1 \]

**Figure 4.8:** WAXD patterns of the OMNC/rPBS nanocomposites.
of the OMNC platelets. However, this OMNC still contains stacks of the montmorillonite platelets, therefore a tiny reflection is seen at $2\theta = 7$. As filler concentration increases, the reflections that related to the interlayer spacing first disappear, then show up again when filler concentration go exceeding 40%. This is a solid evidence that PBS molecules intercalate in between OMNC platelets, thus the interpenetrated networks come out. Therefore, the $d_{020}$ reflection becomes overwhelming comparing to $d_{001}$.

### 4.4 Conclusions

Thus far, an interpenetrated network was manufactured by immersing a skeleton into a soft phase. The resulting structure is resistant to the sustained load, without altering the self-healing characteristics. The organic modifier of the nano clay is a quaternary ammonium salt bearing two hydrogenated alkyl tallows of up to 18 carbon atoms. Such organic modifier ensures a easy dispersion of the OMNC particles into the self-healing PBS matrix, without forming significant particle-molecule interaction. Secondly, the isotropically dispersed OMNC particles form a creep resistant framework, and its creep inhibiting effect, $G'_{0.01}$, is indeed increasing as a function of filler concentration. Thirdly, as a reinforcement, OMNC is able to improve the elasticity of the self-healing PBS matrix $G_0$. Nevertheless, the above mentioned criteria of the OMNC particles make it a desired reinforcement in producing intrinsic self-healing nanocomposites.
Tuning the mechanical properties of a supramolecular elastomer by incorporation of graphene oxide and organically modified graphene oxide

This chapter is for a large part based on:
Z. Liu, L.Y. Chu, S. Sachdeva, L.C.P.M. de Smet, E.J.R. Sudhölter, S.J. Picken, N.A.M. Besseling, Tuning the mechanical properties of a supramolecular elastomer by incorporating graphene oxide and organically modified graphene oxide, under preparation,
5.1 Introduction

Polymer nanocomposites containing plate-like nanoparticles have been extensively researched in the past few decades. Polymers are light weighted and ductile, and can be obtained from nature or via chemical synthesis\textsuperscript{116,117}. Clay nanoparticles are one of the most abundant materials on earth, which are rigid and cheap as compared to most of the polymers. The incorporation of clay nanoparticles in the light weighted polymers may not only efficiently reinforce the properties of polymers, but also lower the price of the resulting products\textsuperscript{118}. However, the rigid nature of clay also effectively diminishes the ductility of polymer, and often leads to a stiff but brittle polymer nanocomposites\textsuperscript{119,120}.

Single layered graphene oxide (GO) nano-sheets are flexible, but the Young’s modulus is relatively high\textsuperscript{121,122}. They can be a good alternative of clay nanoparticles. Although the electrical and thermal properties of GO are largely scarified as compared to graphene due to the defects, its mechanical properties remain applicable. Unlike graphene, which may aggregate into multi-layered stacks, the single layered GO can be easily dispersed and preserved in polar solvents.

Graphene oxide (GO) can be produced by chemically exfoliating the graphite or highly oriented pyrolytic graphite (HOPG). The original Hummer’s method\textsuperscript{123} is considered as an essential milestone. The Hummer’s method has been modified for reasons of safety, environment, yield, etc\textsuperscript{124,125,126}. GO thus produced are single-atom-thick, 2D platelets, which can be easily dispersed in polar solvents. The chemical process causes defects in the basal plane of a graphene platelet. Some $sp^2$ carbon atoms transform into $sp^3$ carbon and attach to hydroxyl, carboxyl and epoxy groups. On the one hand, this causes a decrease of the elastic modulus, thermal conductivity, electrical conductivity, etc. On the other hand, its high aspect ratio, high charge exchange capacity allow GO to participate in self-assembling processes in polar environments.

Currently, GO is often reduced in order to partially recover the properties of graphene. The elastic modulus of reduced GO (rGO) reaches 0.25 TPa, which approaches one fourth the performance of defect-free graphene\textsuperscript{121,122}. Schwamb, et al.
127 and Yu, et al.128 have reduced GO distinctly at 450 °C under N₂ for 60 min127 and vacuum dried at 40 °C for 6 h128, respectively. However, they provided rather similar thermal conductivity data (2.8 ~ 3.9 Wm⁻¹K⁻¹).

GO, rGO and graphene as reinforcement particles have been reported to be more efficient as compared to lamellar clays129,130. Besides their influence on thermal and electrical properties, they have been reported to efficiently increase the Young’s modulus and tensile strength, when they are incorporated in polymers131,132,133. Kim, et al.,134 summarized several polymer nanocomposites, where the Young’s modulus are efficiently improved upon the incorporation of GO or rGO. For example, 0.46% GO in PCL leads to a 50% increase of the modulus135; 2.5% GO in PVA increases the modulus by 128%136; 0.5% rGO in PMMA gives 80% increase in modulus131, and the incorporation upon in-situ polymerization of 2.2% rGO in PDMS results in a 1200% increase in modulus134. All percentages mentioned above are by volume.

Polyborosiloxane (PBS) is a supramolecular elastomer, synthesized by reacting boric acid (BA) with PDMS at elevated temperatures41. Long PDMS chains are cleaved and the unsaturated ends are modified with the borono moieties (B−(OH)₂). Therefore, the molecular structure of a well-refined PBS molecule consists of an apolar siloxane backbone (Si−O−Si) and two polar borono end groups. However, due to chain cleavage reaction, there is always a small fraction of PBS molecules bearing one borono end. We denote the refined PBS “rPBS”41. rPBS is a crystal-clear and colorless viscoelastomer.

In this chapter, we will discuss the behaviour of nanocomposites of rPBS and GO. The rPBS matrix was not simply mechanically stiffened as usual. Instead, it leads to the formation of a thixotropic system. However, when we use GO platelets modified with organic surfactants, the organically modified GO (OMGO) platelets behave as ordinary reinforcement particles.
5.2 Experimental section

5.2.1 Materials

Polyborosiloxane (PBS) was produced by cleaving the poly(dimethylsiloxane) and modifying the unsaturated ends of PDMS with borono groups (−O−B−(OH)$_2$) at elevated temperatures$^{41}$. In this chapter we used the same refined PBS (rPBS6) as introduced in Chapters 2. The number average molar mass of rPBS is about 1600 g/mol. Isopropyl alcohol (IPA) of technical grade (VWR international) is used as solvent for preparing the rPBS based nanocomposites. Graphene oxide (GO) flakes and dimethyldioctadecylammonium chloride (DDA−Cl) were purchased from Graphene Supermarket and Sigma-Aldrich.

5.2.2 Organo-modification of graphene oxide

0.82 g of GO flakes and an excessive amount of DDA-Cl (ca. 1.88 mmol) were separately dispersed and sonicated in 500 ml of demineralized (demi) water, until they formed homogeneous suspensions and dispersion, respectively. We transferred the aforementioned two mixtures into a 2 L round bottom flask and adjusted the total volume to 2 L with demi-water, in order to flatten the GO platelets and increase the degree of modification. This modification process is a modified ion exchange reaction, during which we have stirred the mixture at 60 °C and 400 mbar. The DDA cations bind to the GO surface. The resulting hydrogen chloride evaporates together with some water. After 40 hours, we filtered this mixture with glass microfiber filter paper (pore size ≈ 1.2 /μm, Whatman). The filter cake was washed with demi-water, until the pH value of the filtrate is close to 7. The filter cake was then freeze dried, and we collect a brown fluffy powder in the end.

Several visual observations indicated the success of the surface modification. Firstly, a clear precipitate occurred as we stopped stirring, however a 0.41 mg/ml GO suspension stayed homogeneously for days. Secondly, the 0.41 mg/ml GO suspension passed through the filter paper, but the modified product could not. Thirdly, we collected about 1.28 g of modified product, which is much heavier than the input of GO. More detailed information about this organo-modified GO (OMGO) will be provided in the results and discussion section.
5.2.3 Methods

The rPBS based nanocomposites were prepared by mixing the rPBS/IPA solution with the sonicated particle/IPA mixture, and followed by the removal of solvent at 80 °C. The nanocomposites were all further mechanically homogenized and made into thin films (µm) by a rubber mill at room temperature. The thin films were conditioned under ambient humidity for one week, to recover the borono moieties (B(OH)$_2$) that might be dehydrated into the boroxane (B–O–B) upon solvent removal. After conditioning, we processed the nanocomposites into thin (≈ 30 µm) and thicker films (≈ 1 mm) with the rubber mill, for X-ray diffraction and rheology measurements, respectively.

1 mg/100 ml as-received GO/H$_2$O and OMGO/IPA suspensions were prepared for atomic force microscopic (AFM) investigations. We only shaked the volumetric flasks during dispersion, because we wanted to preserve the original size of GO. Shaking was sufficient to well disperse OMGO in IPA. Silicon wafer was plasma treated under air to increase its surface hydrophilicity. The suspensions were left to rest for 1 day to let the aggregated particles sediment. We took droplets from the top-layer of the suspension and spin-coated these onto the dry silicon wafer at 2000 rpm for AFM investigations.

Thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) was done on a STA 449 F3 Jupiter instrument. Evolved gases were simultaneously analyzed by mass spectrometry. The heating rates for GO and OMGO were 3 °C and 5 °C per min, respectively. Argon was used as protective and purge gas. A Bruker D8 advance X-ray diffractometer was used to examine the interlayer spacing of particles. GO and OMGO were measured in powder form under CoK$_{\alpha}$ radiation ($\lambda$ = 0.179 nm). Fourier Transform Infrared (FTIR) Spectroscopy was performed with a Perkin–Elmer Spectrum 100 series FTIR spectrometer, using the attenuated total reflectance (ATR) mode. Rheological measurements were carried out on a TA AR G2 Rheometer, using the plate–plate geometry: an upper plate of diameter of 40 mm for pristine PDMS, and of 8 mm for the viscoelastic PBSs. X-ray photoelectron
spectroscopy (XPS) was used to identify the presence of elements and surface functionalities of the GO. Atomic force spectroscopy (AFM) was used to visualize the structural difference between a single layered GO platelets and OMGO.

## 5.3 Results

### 5.3.1 Characterization of GO and OMGO

![Figure 5.1: XPS spectrum of as-received GO, and deconvoluted curves corresponding to C–C, C–O, and C=O moieties.](image)

The carbon XPS spectrum of the as-received GO is shown in Fig. 5.1, as well as its deconvoluted fitting curves. The molar ratio of C=O to C–O moieties is estimated from the ratio of their peak areas, which is about 1:5. The molar ratio of carboxyl (O–C=O) to C–O moieties, which include both hydroxyl (C–OH) and epoxide (C–O–C), is estimated to be 1:4. However, besides carbon and oxygen, XPS also revealed the presence of sulfur and chlorine, which must have been introduced into GO during manufacturing. We dialyzed the aqueous GO suspension with demi-water for 24 hours, and examined the dialyzed GO powder with XPS too. Table 5.1 exhibits a summary of the elements that are present in the as-received and dialyzed GOs. We
found that chlorine remained and GO was contaminated unexpectedly by sodium, calcium and silicon elements. We suspect that sodium and calcium atoms may come from the dialyzing membrane and demi-water, while silicon might come from the glasswares. However, the removal of sulfur indicates that sulfur was not covalently bonded to GO. We proceeded with the modification of the as-received GO without dialysis.

<table>
<thead>
<tr>
<th></th>
<th>Atomic fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td></td>
</tr>
<tr>
<td>As-received</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>67.45</td>
</tr>
<tr>
<td>Dialyzed</td>
<td>67.78</td>
</tr>
</tbody>
</table>

Table 5.1: Elements in as-received and dialyzed GOs by means of the XPS investigation.

OMGO platelets are GO platelets covered by hydrophobic alkyl chains. Ideally, we would like to totally insulate the hydrophilicity of GO, in order to confirm that the thixotropic behavior of GO/rPBS nanocomposites is indeed due to the surface properties of GO.

Figure 5.2 (a) shows the FTIR spectra of GO, DDA-Cl and OMGO. The peak at 1620 cm\(^{-1}\) corresponds to the C\(=\)C skeletal vibrations of unoxidized graphitic domains, which is not influenced by the ion exchange modification\(^{138}\). Therefore, we normalized the spectra of GO and OMGO to this peak for better comparison. The other peaks at 1050 cm\(^{-1}\), 1380 cm\(^{-1}\) and 1730 cm\(^{-1}\) can be assigned respectively to the vibration of C–O in epoxy, O–H in C–OH and carboxyl groups, and C=O in carboxyl groups and carbonyl moieties. The broad band at \(ca.\) 3200–3440 cm\(^{-1}\) is due to the vibration and stretching of O–H in C–OH, carboxyl groups, and intercalated water molecules.

We applied thermogravimetric analysis (TGA) to study the thermal stability of our chemicals. Components emitted during the thermal measurement were analyzed via mass spectrometry. Figure 5.2 (b) shows the decreasing weight of samples as a function of temperature. Thermal decomposition of GO has been reported to take place in four steps\(^{139}\). It releases superficially sorbed water below 120 °C, and then emits a mixture of CO\(_2\), CO and H\(_2\)O between 120 and 190 °C. Further degradation
in the temperature range of 190 to 300 °C releases a mixture of CO₂, CO, H₂O and SO₂. The formation of H₂O and SO₂ is due to the decomposition of −SO₃ moieties
such as sulfuric acid, which was used in the synthesis of GO\textsuperscript{123}. Above 300 °C, CO becomes predominant in the emission. Here, we will compare and interpret the thermal decomposition of our GO and OMGO in the same stepwise way with one additional step between 300 and 480 °C. Table 6.1 contains the weight loss of GO and OMGO in each step. Step 1 and 5 indicate the release of superficially adsorbed water and CO, respectively. In step 2, OMGO emits only half amount as compared to GO, because the carboxyl (COOH) and alcohol (COH) groups that have contributed to the ion exchange reaction are preserved. A rough estimation is thus made that half amount of the carboxyl and hydroxyl groups participate in the ion exchange reaction. DDC-Cl is thermally stable in step 2, too. GO and OMGO behave most differently in step 3 and 4, because modifier molecules start decomposing and totally vanish by the end of step 4. GO releases a mixture of CO\textsubscript{2}, CO, H\textsubscript{2}O and SO\textsubscript{2} in step 3, and emits CO from step 4 onward at a constant rate (see the slope). However, OMGO undergoes a rapid weight loss in step 3 and 4, where the degradation of GO and modifier occur both. From step 5 onward, OMGO loses weight in the same rate as GO, which indicates the modifier is completely gone. rPBS possesses outstanding thermal stability, its weight remained unaltered unless heated above 300 °C.

In OMGO, the incorporation of modifier decreases the content of GO. As a consequence the mass fraction of the final residue of OMGO is much lower than that of GO. Together with the consideration of the superficially sorbed water, we estimate the mass fraction of the modifier is around 0.45. Such a high content of modifier was confirmed by the mass increase observed during the preparation of OMGO, where we started with 0.8 g of GO and harvested 1.28 g OMGO. If we correct for the 7.5% sorbed water out from as-received GO, the calculation confirms that OMGO consists of at least 43% modifier.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Step 1 (T_{room}) to 120 °C</th>
<th>Step 2 to 190 °C</th>
<th>Step 3 to 300 °C</th>
<th>Step 4 to 480 °C</th>
<th>Step 5 to 900 °C</th>
<th>Final %</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>7.5</td>
<td>28.3</td>
<td>11.5</td>
<td>5</td>
<td>12.1</td>
<td>35.6</td>
</tr>
<tr>
<td>OMGO</td>
<td>3</td>
<td>14.3</td>
<td>27.4</td>
<td>22.3</td>
<td>13.4</td>
<td>19.6</td>
</tr>
</tbody>
</table>

**Table 5.2:** Weight loss of GO and OMGO samples during the TGA measurements.
We show the morphology of the as-received GO and OMGO via AFM images in Fig. 5.3. GO platelets are single-atom thick and several $\mu$m$^2$ in area. AFM reveals the single-atom thickness of GO with an identical height ($\approx 0.9$ nm). The exfoliated OMGO platelets have much smaller areas, most likely due to the sonication step in their preparation. The thickness of a single OMGO layer has increased to roughly 2 nm due to the surface modification. Regarding the number of carbon atoms in a DDA molecule, we conclude that most of the modifier molecules lie down on the GO surface. The AFM image of OMGO shows many bright spots, which indicates a different thickness of about 5 nm. As this corresponds to about twice the thickness of a OMGO platelet, these might correspond to small OMGO fragments stacked on a bigger platelet. The image of OMGO is less clear than that of GO, such difference indicates the surface of the platelets becomes softer owing to the presence of modifiers.

We compare the WAXD spectra of GO and OMGO in Fig. 5.4. GO shows a symmetric peak at $2\theta = 12.5^\circ$, which indicates an average interlayer spacing of about 0.82 nm between the GO sheets according to Bragg’s law$^{140}$. In OMGO, the intercalation
of modifier molecules expands the distance between platelets. As a result, we see two new peaks centered at $2\theta = 9.1^\circ$ and $6.0^\circ$ in the spectrum of OMGO. The related interlayer spacings are 1.14 nm and 1.7 nm, respectively.

### 5.3.2 The formation of thixotropic nanocomposites due to the incorporation of GO

Incorporation of GO platelets in rPBS leads to an extraordinary softening phenomenon. During sample preparation, we observed that a tiny inclusion of GO at a mass fraction of 0.001 (0.1% by weight) readily softened rPBS. For a mass fraction of 0.01, the resulting nanocomposite exhibited as a thin liquid. Figure 5.5a shows the dynamic shear moduli $G'$ and $G''$ of the GO/rPBS nanocomposites with 0.1% w/w and 1% w/w GO inclusion as a function of strain. For 0.1% w/w GO/rPBS nanocomposite, the $G''$ curve is always larger than the $G'$ curve, and they are flat until the %strain reaches about 4 decades. The $G'' > G'$ relation indicates that the viscous properties are predominant under the measurement conditions. The flat curves reflect the linear

Figure 5.4: WAXD spectra of GO and OMGO. GO and OMGO were measured in the powder form and the corresponding interlayer spacing was calculated based on the Bragg’s Law. The interlayer spacings are 1.14 nm and 1.7 nm, respectively.
Figure 5.5: Dynamic shear moduli of rPBS and GO/rPBS nanocomposites, (a) measured in strain sweep procedure at a constant frequency of 10 rad/s, (b) measured in frequency sweep procedures. (c) Dependency of steady shear rate upon stress. (d) Time sweep curves of 1% GO/rPBS nanocomposite measured at 0.1% strain and 10 rad/s after 1 min of vigorous pre-shear. All frequency sweeps were done at 20 °C and 1% strain, except for the 1% GO/rPBS nanocomposite (0.1% strain) viscoelastic behaviour of the inspected nanocomposite, which enters the non-linear viscoelastic regime at a %strain of about 40. In contrary, the 1% w/w GO/rPBS nanocomposite behaves non-linearly already at a very small strain (∼10⁻³%). Aiming at measuring the dynamic moduli of samples in their linear viscoelastic regimes, we used 1% strain for rPBS and 0.1% w/w GO/rPBS nanocomposite, but 0.1% strain for 1% w/w GO/rPBS nanocomposite. Figure 5.5b exhibits the dynamic shear moduli of samples as a function of oscillatory frequency. The frequency, at which G’ and G” curves intersect, inversely equals the terminal relaxation time, τ₁. The G’ and G” curves of rPBS and 0.1% w/w GO/rPBS nanocomposite strongly dependent on frequency. The rheological behavior can be accounted for with the Maxwell model
where viscous and elastic properties respectively dominate below and above $1/\tau_1$. For the 1\% GO/rPBS nanocomposite, $G'$ and $G''$ are constant at low frequencies, which noticeably increase above 3 rad/s and interest at about 80 rad/s. Such evolution of $G'$ and $G''$ could be referred to the standard linear solid (SLS) model, which is constructed by connecting a separate spring in parallel to a Maxwell unit. In the SLS model, there are two plateaus located at high and low frequencies, where the $G' > G''$ relation is valid. Between these two plateaus, $G''$ values are larger than the $G'$ values. The constant $G'$ and $G''$ might be corresponded to the low frequency plateau, and the intersection is the entrance to the $G'' > G'$ region in the SLS model. A speculation is therefore that if the measurement on the 1\% w/w GO/rPBS nanocomposite can be done at higher frequencies, $G'$ will increase and show another plateau. The $G' > G''$ relation indicates that the 1\% w/w GO/rPBS nanocomposite is in fact a solid, although it is quite weak.

$G'$ of the 0.1\% w/w GO/rPBS nanocomposite drops above 40 rad/s. This may either be due to an experimental error, or indicate a non-linearly behavior.

We also investigated the 1\% GO/rPBS nanocomposite with steady shear procedures, because it can be handled as a thin liquid. The shear rate vs. shear stress plot in Fig. 5.5c clearly demonstrates that the 1\% w/w GO/rPBS nanocomposite is shear thinning. The inserted graph in Fig. 5.5c shows the same plot in a limited shear stress range, which implies the presence of a yield stress. Apparently, the 1\% w/w GO/rPBS nanocomposite behaves neither as a perfect Newtonian fluid, nor a typical shear thinning material. It seems to firstly yield at a small stress and then become thinning at higher stresses, therefore we employed the Hershel-Bulkley equation.

\[ \sigma = \sigma_Y + \kappa \cdot \dot{\gamma}^n \]  

Equation 5.1 shows the expression of the Hershel-Buckley equation, where $\sigma$, $\sigma_Y$ and $\dot{\gamma}$ represent the shear stress (Pa), yield stress (Pa) and shear rate (1/s), respectively. $\kappa$ and $n$ are empirical constants. The Hershel-Bulkley model fits the experimental results precisely, and provides us with a yield stress of about 19 Pa. The two fitting constants are $\kappa = 4.5$ and $n = 0.7$. 
The dynamic shear moduli of the 1% w/w GO/rPBS nanocomposite was followed in a time sweep procedure, prior to which the sample was vigorously pre-sheared at 1000 rpm for 1 min. Figure 5.5d shows the evolution of the dynamic shear moduli as a function of operation time, where pre-shear was stopped at \( t = 0 \) s. Apparently, the mechanical properties recover over time. The \( G' \) and \( G'' \) approach to plateau values after 1 h, which roughly equal the frequency independent moduli shown in Fig. 5.5b (green curves).

Figure 5.5a shows that the 1% w/w GO/rPBS nanocomposite behaves non-linearly at very small strains. Figure 5.5c confirms the 1% w/w GO/rPBS nanocomposite is a weak solid below a shear stress of 19 Pa, but will be a shear thinning fluid when it is subject to medium shear stress. Figure 5.5d shows the weakened properties due to vigorous pre-shear can be recovered in time. However, in the linear viscoelastic regime, the 1% w/w GO/rPBS nanocomposite behaves as a solid. All together, we conclude that the 1% w/w GO/rPBS nanocomposite in fact is thixotropic. GO/rPBS nanocomposites of higher GO content (5 ∼ 10% w/w) were also investigated, however the increasing GO content did not significantly increase the mechanical performance of the nanocomposites.

Figure 5.6: Graphic demonstrations of a. the crystal-clear and colorless rPBS, b. fluidic 1% w/w GO/rPBS nanocomposite transferred with a syringe, and c. rubbery 1% w/w GO/rPBS nanocomposite after dehydration at 150 °C and 400 mbar for 2 h.

More over, such thixotropic nanocomposite can be reversibly hardened upon thermal treatment. Figure 5.6 shows the appearance of rPBS, 1% w/w GO/rPBS and
Tuning the mechanical properties of a supramolecular elastomer by . . .

Figure 5.7: Dynamic shear moduli of dehydrated 1% w/w GO/rPBS nanocomposite, and the evolution of the storage modulus of an dehydrated sample in ambient humidity as a function of time measured at 0.1% strain and 10 rad/s.

dehydrated 1% w/w GO/rPBS, which was preserved at 150 °C and 400 mbar for 2 h. The crystal–clear supramolecular elastomer rPBS was molded into a pine tree shape and shown in Fig. 5.6a in black frame. The 1% w/w GO/rPBS thixotropic nanocomposite is a black thin liquid, which is transportable with a syringe through a needle (Fig. 5.6b in the green frame). The dehydrated 1% w/w GO/rPBS nanocomposite is shown in a blue frame in Fig. 5.6c. Apparently, dehydration has converted the thixotropic nanocomposite into a self-standing elastomer.

We provided the dynamic shear moduli of the dehydrated 1% w/w GO/rPBS nanocomposite in Fig. 5.7. Both $G'$ and $G''$ are much larger than the thixotropic nanocomposite. The frequency, at which $G'$ and $G''$ curves intersect, equals the inverse of the terminal relaxation time, $\tau_1$. The dehydrated sample shows a larger $\tau_1$ as compared to rPBS as well. Referring to the book of Rubinstein and Colby\textsuperscript{109}, the higher modulus is related to a higher density of cross-links. The larger $\tau_1$ value is an indication of less molecular mobility. In combination, it confirms that dehydration leads to an increased density of cross-links in the 1% w/w GO/rPBS nanocompos-
ites. The inserted plot in Fig. 5.7 was made by following the storage modulus of the dehydrated sample at ambient humidity. Clearly, $G'$ decreases over time. We attribute this deterioration in storage modulus to the hydrolysis of the cross-linker. Water molecules from the environment will penetrate and hydrolyze the hardened sample towards a liquid again.

### 5.3.3 The ordinary reinforcing effect of OMGO platelets

We show the dynamic shear moduli of the OMGO/rPBS nanocomposites as a function of frequency in Fig. 5.8a. $G'$, $G''$ and $\tau_1$ are generally increasing as the filler content increases. Although $G'$ and $G''$ of the 1% w/w OMGO/rPBS nanocomposite are smaller as compared to rPBS, the $\tau_1$ is bigger than that of rPBS. This indicates that the incorporation of OMGO platelets readily weakens the mobility of the PBS molecules at 1% w/w. We observe the appearance of a second plateau of the storage modulus curves at low frequencies ($\omega < 0.01$). Gong\,\textsuperscript{142} has introduced a double-network gel system, in which one hydrogel network interpenetrates through the network of another hydrogel. In such a duel-network hydrogel, the mechanical performance has been greatly improved. Therefore, we suggest that OMGO platelets may have formed a skeleton within the dynamically cross-linked PBS medium. The presence of such skeleton prevents the nanocomposites from creeping under sustained load, which is a deformation happening in long time scale.

We have plotted the moduli at the high frequency plateau ($G_0$) and the lowest measurement frequency ($G_{\omega=0.01}$), together with the $\tau_1$ values as a function of the OMGO mass fraction in Fig. 5.8b. $G_{\omega=0.01}$ can be considered as a measure of the extra modulus that the OMGO network has contributed to the elasticity of the nanocomposites. $G_0$ represents the overall elasticity of the nanocomposite. Increasing the mass fraction of OMGO leads to a continuous increase in $G_{\omega=0.01}$, however, a reduction in $G_0$ at low OMGO content. This might be due to the competition between the formation of OMGO network and the loss of PBS cross-links. OMGO particles form network and contribute to the overall elasticity of the nanocomposites on the one hand. On the other hand, cross-links between PBS molecules are largely deceased, because the high aspect ratio OMGO particles are efficient in isolating the
Tuning the mechanical properties of a supramolecular elastomer by...

Figure 5.8: a. Dynamic moduli of rPBS and OMGO/rPBS nanocomposites as a function of frequency. b. A summary of the moduli at high ($G_0$) and low ($G_{\omega=0.01}$) frequencies, as well as $\tau_1$ as a function of the OMGO mass fraction.

PBS molecules. At low OMGO content, the OMGO network does not provide significant elasticity to compensate the loss in the overall elasticity due to the isolated
PBS molecule. Therefore, \( G_0 \) decreases at first. The contribution originated from the OMGO network quickly increases and plays a predominant role above the OMGO mass fraction of 0.01. The evolution of \( \tau_1 \) values confirms that PBS molecules becomes less mobile as the content of OMGO increases.

![Graph showing shear rate vs. shear stress](image)

**Figure 5.9:** Dependency of steady shear rate upon stress. The mass fraction of OMGO in the nanocomposites is 0.01.

Figure 5.9 shows the shear rate vs. stress relations of rPBS and the 1% w/w OMGO/rPBS nanocomposite. The plot of rPBS can be perfectly fitted with a linear curve through the origin. It thus confirms that rPBS behaves as a Newtonian fluid. The plot of 1% w/w OMGO/rPBS nanocomposite seems to be linear and across the origin as well. However, it bends downwards at the shear stress of about 40 Pa in the inserted plot. The linear fitting curve through origin in the inserted plot only manages to fit the first a few points on the plot of 1% w/w OMGO/rPBS nanocomposite. Such behavior meets the criteria of a shear thickening material.
5.4 Discussion

Formation of the GO/rPBS thixotropic nanocomposites is a unique phenomenon occurring upon combining PBS with GO. A PBS molecule has a hydrophobic siloxane backbone and two hydrophilic borono end groups (B(OH)$_2$), because of which the PBS molecules form a 3D network via hydrogen-bonds (HBs) and reversible boroxane bonds (B–O–B)$^{41}$. GO is rich in surface polar moieties.$^{143,144,145}$

The incorporated GO platelets in the rPBS matrix, not only efficiently hinder the PBS molecules from cross-linking due to their large surface area, but also immobilize the isolated PBS molecules upon forming weak GO-PBS HBs. Thus, the number of strong PBS cross-links decreases, and therefore it results in weak nanocomposites. The weakening effect can be related to a combination of a few mechanisms, such as particles interrupted chain packing$^{146}$, reduced entanglement density$^{147}$, increasing in the free volume$^{148}$, slip between particle and molecules$^{149}$, selectively adsorption of long molecules at particle surface$^{150}$, and formation of depletion layer around the organic nanoparticles$^{148,151}$. Noticeably, despite the reversible boroxane bonds, the PBS-PBS HBs are also stronger than the GO-PBS HBs, Because boron is a better electron donor than carbon. The hydroxyl groups on a trigonal boron is a stronger HB acceptor than the hydroxyls on carbon (Fig. 5.10 (a) and (c)). In ambient environment, a trigonal boron may dynamically and reversibly transform into a tetrahedrally configured boron, which is an even stronger HB acceptor (Fig. 5.10 (b)). Consistently, the GO/rPBS nanocomposite reaches the lowest stiffness at a mass fraction of 0.01, because the PBS-PBS cross-links are reduced to the greatest extent. A further increase in GO loading causes GO platelets to stack, which only decreases the aspect ratio of GO without significantly reducing the total surface area of GO. As a result, the PBS molecules are still isolated from each other and the GO-PBS HBs are predominant. Therefore, the 5% and 10% w/w GO/rPBS nanocomposites are still viscous liquid.

Further more, this liquid nanocomposites can be transformed into a self-standing elastomer upon dehydration, as condensation can occur between a fraction of borono groups (PBS) and the polar groups of GO at elevated temperatures. It thus leads to a solid composite, in which the outstanding mechanical properties of GO are able to
take over and function. As the condensation reaction is reversible, it guarantees a reversible liquid-solid transformation.

**Figure 5.10:** Schematic representations of the hydrophilic groups attached on PBS (A and B); hydrophilic groups on the surface of GO (C); and the structure of a single OMGO layer (D).

Although the presence of OMGO platelets also softens PBS at low content, the mechanism is distinct from that of the GO/rPBS system. Figure 5.10 (d) represents a fraction of a OMGO sheet. We draw the standing two-tallow modifier molecules only for representing structure of OMGO more understandably. In reality, AFM technique proved that the modifier molecules actually lie down on to the surface of GO (Fig. 5.3). OMGO platelets also soften the rPBS matrix at low concentration, but the mechanism is to interrupt the PBS network primarily as inert obstacles. At higher loadings, modifier molecules facilitate OMGO platelets to form a secondary network via entanglement, which induces a second relaxation process towards longer time scales. The increasing $\tau_1$ as a function of OMGO concentration suggests a significant PBS-OMGO interaction. We propose that the modifier molecules have not only made a major contribution in establishing the filler framework, but also actively confined PBS molecules.
5.5 Conclusions

The GO/rPBS nanocomposites show unique thixotropic behaviour above a 1% \textit{w/w} GO content. We suggest that GO platelets can efficiently interrupt the PBS network and confine the isolated PBS molecules by forming PBS-GO interaction. The loss of dynamic PBS cross-link therefore results in softened nanocomposites. On the one hand, the weak PBS-GO hydrogen bonds keep these nanocomposites thixotropic in bulk. Under stress, these nanocomposites become thin liquids. The PBS-GO hydrogen bonds can be converted into covalent bonds upon dehydration. Thus, we can tune the condition of these nanocomposites reversibly between liquid and solid states, by dehydration and hydrolysis. The organically modified GO platelets do not show polar moieties at the surface, therefore, they function as ordinary reinforcement particles.
A brief overview: the influence of filler morphology on the performance of Polyborosiloxane based self-healing nanocomposites.
6.1 Introduction

In general, a composite consists of an adhesive body and ingredients. The inclusion of an ingredient normally may bestow the adhesive body with particular properties, such as mechanical enhancement\textsuperscript{152,153,154,155}, electrical or thermal conductivity\textsuperscript{63,156,157}, piezoelectrical properties\textsuperscript{158}, etc. Thus, the properties of a commercially available and socially accepted product become tuneable. Along the development of the composites, the filler/matrix compatibility, filler geometry and morphology were found to be essentially important for manufacturing the composites.

Filler/matrix compatibility may reflect the homogeneity of the composite system, as well as the efficiency of the filler incorporation. A bad filler/matrix compatibility will easily cause the separation of filler phase from the matrix phase by means of filler aggregation and accumulation. Thus, the specific functionality of the filler particles can not be applied evenly and efficiently throughout the matrix body. However, a good filler/matrix compatibility does not always guarantee an advantage. In chapter 5, we have discussed the unique softening behavior of the GO/rPBS system, although such combination provides us with an exciting liquid-solid transformable composite system.

Apart from the compatibility, filler geometry and the morphology they exhibit in the composites are equally important. Filler geometry refers to the appearance of filler particles in the well-exfoliated form. They are generally categorized into 0D (spheres and cubes), 1D (rods, fibers and wires) and 2D (sheets and flakes) particles. Morphology in material science commonly studies the size, shape, texture and phase distribution of a physical object. In practical, filler particles that are participating in a polymer composite may exhibit distinct morphology and geometry, due to unideal mixing, dispersion, intercalation, or other uncertainties. Here we may assume an extreme case to interpret the difference straightforwardly, 2D clay platelets may form thick stacks towards 0D filler due to insignificant intercalation.

Such reduction in shape factor (2 times the ratio of long dimension to short dimension) of filler particles can not be directly visualized, unless X-ray diffraction, SEM, TEM or other similar techniques are employed. Alternatively, we may use the
mechanical models to roughly estimate the average shape factor of the composite, such as the Halpin-Tsai mechanical model. When the filler concentration is not far beyond the percolation threshold, at which filler network starts providing a secondary contribution to the mechanical performance of the composite, Halpin-Tsai model can rather precisely describe the change of shape factor as a function of filler content. At very low filler content, particles are assumed to be well intercalated and isotropically orienting (exfoliate) without touching one another. As the filler content starts approaching to the percolation threshold, particles may not be adequately intercalated but locally orienting due to the spatial constraints, which leads to a reduction of shape factor. Above the percolation threshold, Halpin-Tsai model may provide an increasing shape factor, which seems unreliable with respect to the more compact structure. However, it may also suggest that the aggregates of particles start bridging and forming more pronounced network.

Similarly, rheology can be a measure of the mechanical performance of a composite, such as elasticity and viscosity. When combined with mechanical analogous models, it is also capable of reflecting the mobility and microscopic structures of a polymer composite. Maxwell model and Kelvin-Voigt model represent the two extreme behaviors of viscoelastic materials in theory as pure elastic and pure viscous. However the performance of all practical viscoelastomers fall between them. Then the mechanical analogs can be expanded accordingly to attribute the change of bulk properties to specific analogous units, such springs and dashpots.

In this chapter, we briefly summary all the composite system that we have been working on. We will focus on discussing the influence of surface properties, geometries and content of filler particles on the performance of the resulting composites.

6.2 Chemicals

rPBS6 serves here as matrix material for all composites. 0D fillers used are boric acid (BA) BP168-1 (Acros Organics BVBA, Geel, Belgium.), and EMForce® Bio additives (Specialty Minerals Inc.). EMForce® Bio additives are made of calcium carbonate core and a surface layer of modifier. 1D filler is multi-wall carbon nanotubes (CNT), under trade name Nanocyl™ NC 7000 (Nanocyl). 2D fillers are mainly clay
based platelets, such as Nanofil® 116, Cloisite® 30B, Clayton® APA from southern clay products Inc. Details of IPA, Cloisite® 20A, GO and GO derivatives can be referred to earlier chapters.

### 6.3 Methods

Composites that will be mentioned in this chapter were prepared in the same way as the Cloisite 20A/rPBS, GO/rPBS nanocomposites. Filler powder was firstly weighed and then sonicated in the IPA medium with the bath sonicator for 3 hours. rPBS6 was then added into the filler/IPA mixture. We stirred the new system with magnetic stirrer until rPBS6 was all dissolved. The mixture was heated to the boiling point of IPA while stirring. We stopped heating when the system became gelling due to a major removal of IPA. The cooled thick mixture was processed by the rubber-mill for further removal of IP and homogenization. Nanocomposites were firstly compressed into thin film (µm) and conditioned under ambient humidity for one week. In this conditioning step, we aimed at hydrolyzing the boroxane moieties that might be formed during IPA removal. The conditioned samples were again processed by the rubber-mill into thick films for rheological investigations.

The BA/rPBS composite was a litter different, as BA dissolved in IPA, instead of dispersing. We will discuss the interesting behavior of the BA/rPBS composites in the coming section.

### 6.4 Results and Discussion

Composites produced by combining rPBS6 with a wide variety of fillers, were investigated primarily by rheology. We intend to interrupt the rheological behavior of these composites by means of accounting for the interaction between filler particles and the PBS molecules.
6.4.1 0D filler incorporated composites

Filler mass fraction was selected as 0.2, which is commonly used in the composites containing calcium carbonate based additives. The size of the calcium carbonate aggregates around this specific concentration is appropriate for weakening the crack propagation, in order to efficiently toughen the composites. Figure 6.1 exhibits the $G'$ and $G''$ of composites containing 0D fillers, measured in frequency sweep procedure (FSP). As expected, 0D fillers are not efficient reinforcement particles due to their limited shape factor, such as EMF® Bio additives. BA reinforces rPBS6 in a distinct way, because the incorporated BA can actually cross-link with the borono groups of PBS molecules, either by forming H-bonds or reversible boroxane structures. The BA/rPBS composite in fact shows a broadened $G''$ curve. Refer to Chapter 3, to the rheology of the severely dehydrated rPBS, the broadened $G''$ curves of BA/rPBS has confirmed the increased number of cross-links by the added BA.

![Figure 6.1](image-url) **Figure 6.1:** A summary of the oscillatory moduli of PBS based composite with 20% 0D fillers.

Additionally, the BA/rPBS composites also showed a quick reversible clear-opaque transition. As shown in Fig. 6.2a, we obtained a transparent film by heating the
opaque 20 % BA/rPBS composite at 100 °C for 5 minutes. Referring to our knowledge, we attribute the transition to the formation of boroxane moieties, upon which BA molecules cross-link with PBS molecules. The transparent film quickly absorbed humidity from air and turned opaque again (Fig. 6.2b), due to the hydrolysis of the boroxane structure. Figure 6.2c shows the reversibility and rapid response, because the film can recover its transparency by being heated again.

6.4.2 1D multi-wall CNT incorporated nanocomposites

![Graph showing oscillatory moduli of PBS based nanocomposites.](image)

**Figure 6.2:** Oscillatory moduli of PBS based nanocomposites, containing up to 40% 1D CNT particles.

Unlike the 0D particles, which possess limited aspect ratio, the 1D filler can readily show their efficiency in reinforcing the properties of the polymer matrix at rather low filler content. Multi-wall CNT is excellent in mechanical, thermal and electrical properties, but relatively cheap in price. Figure 6.2 exhibits the reinforcing effect of the CNT in the rheological properties of rPBS6. An addition of 0.1% CNT already leads to a bigger $G_0$, a longer $\tau$, and a second relaxation process at low frequency ($G_\omega=0.01$). As seen in the rheology of the 10% and 40% CNT/rPBS nanocomposites, not only the first two parameters will generally increase as a function of filler
A brief overview: the influence of filler morphology on the... 91

concentration, but also the second relaxation process becomes more and more pronounced. The rheology of the 40% CNT/rPBS nanocomposite demonstrates that this nanocomposite already behaves as a real solid, as $G'$ and $G''$ are no longer frequency dependent.

![Graph showing modulus vs. filler mass fraction](image)

Figure 6.3: Plateau moduli obtained at the highest ($G_0$) and low ($G_{\omega=0.01}$) operational window of the rheometer as a function of CNT mass fraction.

Figure 6.3 shows correlation of the plateau moduli obtained at the highest and low operational frequency window of the rheometer as a function of CNT mass fraction. As discussed in chapter 4, $G_0$ represents a comprehensive properties, which accounts for the plateau modulus of the filler incorporated nanocomposite as a whole. At low filler concentrations, $G_0$ only represents the modulus of rPBS6. The reinforcement of the well-dispersed particles to rPBS6 is negligible, because the modulus of rPBS6 is much weaker than the modulus of most of the filler particles. However, $G_{\omega=0.01}$ primarily refers to the rheological properties of the filler-assembled skeleton. The "$G_{\omega=0.01}$ vs. $\phi$" relation indicates that CNT forms percolated network at a very low filler content (~0.1%), which does not immediately boost the performance of the nanocomposite. The "$G_0$ vs. $\phi$" relation suggests the percolated network starts to sig-
significantly enhancing the nanocomposite above a filler content of about 2%.

The most pronounced difference of the CNT/rPBS nanocomposites from the 2D filler incorporated nanocomposites is that CNT already efficiently enhanced the rheological properties of rPBS6 at 0.1% loading. However, in every clay based nanocomposite system, clay particles will first lower the G' and G", until the filler concentration is beyond the percolation threshold of each particular system. We would attribute such distinct difference to the 1D structure of CNT. The high aspect ratio of CNT allows CNT to form percolated network at low filler concentration, however the limited total surface area of CNT hardly hinders the cross-linking of PBS molecules.

6.4.3 2D clay and its derivatives incorporated nanocomposites

We summarized the rheology data of the nanocomposites that contain clay or clay derivatives in Fig. 6.4. Nanofil 116 are natural clay particles. The rest three are clay derivatives.

As compared to the GO/rPBS thixotropes, Nanofil 116 particles have similar effect due to their hydrophilic surface. However, they work less efficiently than GO platelets, because clay surface possesses less hydrophilic groups than the commercial GO. Figure 6.4a shows that addition of Nanofil 116 leads to a softened nanocomposites, which eventually behaves as a paste at a filler mass fraction of 0.6. τ increases as expected, due to the confinement of the hydrophilic surface to PBS molecules.

Figure 6.4b, c and d show the rheology date of Cloisite 30B/rPBS, Claytone APA/rPBS and Cloisite 20A/rPBS nanocomposites, respectively. As we have realized that a softening effect always accompanies the 2D filler incorporated PBS nanocomposites, until the reinforcement of particle network compensates the loss owning to particle hindered PBS cross-link. In Fig. 6.4b, such compensation is not happening until the filler content reaches 40%. Figure 6.4c and d indicate that in the Claytone APA/rPBS and Cloistie 20A/rPBS nanocomposite, such compensation is readily noticeable around a filler content of 10%. Nevertheless, τ in the above mentioned three nanocomposites is generally unaltered. The unaltered τ can be account for by the surface modification, due to which the hydrophilicity at the clay surface is deactivated.
Thus PBS molecules are no longer confined to the clay surface, therefore $\tau$ is not significantly influenced.

We believe the filler content, at which the enhancing effect of particle is overcoming the softening effect, is also due to the surface modification. However, we are still looking for an convincing clue.

![Figure 6.4: Oscillatory moduli of PBS based nanocomposites, containing MMT based 2D filler particles.](image-url)

We again summarized the $G_0$ and $G_{\omega=0.01}$ as a function of filler mass fraction in Fig. 6.5. Figure 6.5a exhibits a very contrast to the softening effect as the filler content increases. The modulus of the filler network in deed increase as a function of filler content. But the overall modulus of the nanocomposites decreases. In Fig. 6.5b, the Claytone APA/rPBS nanocomposites show similar plots as compared to the Cloisite
20A/rPBS nanocomposites, because the particle have the same surface modifier.

![Figure 6.5: Plateau moduli at the highest ($G_0$) and lowest ($G_{0.01}$) operational window of the rheometer as a function of filler mass fraction. A and B are systems containing Nanofil 116 and Claytone APA, respectively.](image)

We fitted all the $G_0$ vs. $\phi$ and $G_{\omega=0.01}$ vs. $\phi$ curves with power law, and summarized the fitting parameters in Tab. 6.1 (refer to chapter 4). $k$ and $\alpha$ are the coefficient factor and power exponent.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G_0$ (Pa)</th>
<th>$G_{0.01}$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>6E7</td>
<td>1E8</td>
</tr>
<tr>
<td>Nanofil 116</td>
<td>1E5</td>
<td>2E4</td>
</tr>
<tr>
<td>Cloisite 30B</td>
<td>7E6</td>
<td>6E6</td>
</tr>
<tr>
<td>Cloisite 20A</td>
<td>6E7</td>
<td>5E7</td>
</tr>
<tr>
<td>Claytone APA</td>
<td>2E7</td>
<td>2E7</td>
</tr>
<tr>
<td>OMG0</td>
<td>1E6</td>
<td>4E5</td>
</tr>
</tbody>
</table>

Table 6.1: Summary of the power law fitting parameters originating from the modulus vs. filler mass fraction curves.

### 6.5 Conclusions

In this chapter, we have discussed the rPBS6 based nanocomposites, containing filler particles of different geometries. One of the highlighted issues is that filler particles
do not efficiently reinforce the rPBS6 matrix at low filler concentration, because the rPBS6 matrix is too weak to take advantage from the individually dispersed robust particles. So the filler particles will soften rPBS6, rather than enhancing, by hindering the PBS cross-links. Filler particles may form network above certain percolation threshold, which is dependent on particle geometry. Such network will provide pronounced contribution to overcome the loss due to less cross-linked PBS. Surface properties of the filler particles plays an essential role in the properties of the nanocomposites, in which they participate. Particles that possess hydrophilic groups will form weak H-bonds with PBS molecules and lower their mobility. Thus the nanocomposites will exhibit a longer terminal relaxation time, but a weakened mechanical performance.
Bibliography


Summary

The aim of this thesis is to execute a bottom-up design of the intrinsically self-healing nanocomposites. We briefly introduced the self-healing materials in chapter 1, covering classification and basic self-healing mechanism. We decided to interpret the viscoelastic properties of the materials in the following chapters primarily with mechanical analogous, which may contain individual model unit (spring or dashpot) or a combination of a few model units in specific alignment. We also introduced the detailed mathematic derivations of these mechanical analogous up to three units (2 springs and 1 dashpot), both as dynamic ($G(\omega)$) and steady state ($J(t)$) functions.

In chapter 2, we have synthesized polyborosiloxane (PBS) according to the last century recipe as the self-healing supramolecular matrix. Additionally, we provided the long existing recipe with exclusive supplementary details, such as reaction kinetics, structural refinement and characterization, mechanical performance, glass transition temperature, etc. We have denoted the refined PBS, in which the end groups of PBS primarily exhibit in the well-defined borono structure ($B-(OH)_2$), rPBS.

In chapter 3, the molecular interaction of PBS molecules that leads to the self-healing behavior was investigated with modern techniques. Besides the well-known physically cross-linked H-bonds, PBS molecules also cross-link via forming reversible covalent boroxane structures ($B-O-B$). At ambient conditions, the boroxane moieties prefer to form a trimeric ring, which is denoted "Boroxine". Solid state MAS $^{11}$B NMR spectrum indicates that $sp^2$ hybridized trigonal boron atoms and $sp^3$ hybridized tetrahedral boron atoms coexist in PBS at ambient conditions. Upon severe dehydration, the quantity of boroxane moieties increases at a cost of the borono groups. The $sp^3$ boron to $sp^2$ boron ratio increases as well. Hydrolysis of the boroxane moieties can automatically occur in ambient humidity, and it recovers supramolec-
ular nature of rPBS.

Chapter 4 and 5 focus on the reinforcing effects of rigid nanoclay particles (Cloistie 20A) and flexible graphene oxide (GO), respectively. As PBS molecules bear the hydrophilic borono end groups, the incorporation of natural clay and graphene oxide leads to softened nanocomposites due to their hydrophilic surfaces. GO platelets efficiently drive the GO/rPBS nanocomposite into thixotropic material readily at a mass fraction of 0.001. Increasing the mass fraction of GO to 0.01, it results in a very thin thixotropic fluid. However, natural clay surface is not as hydrophilic as GO. The softening effect is not only less pronounced, but also quickly compensated due to the formation of the particle network. Nevertheless, it results in a paste-like thixotrope when the mass fraction of natural clay reaches 0.6. Cloisite 20A and OMGO are surface modified natural clay and GO, with almost the same alkyl modifier. They behave as ordinary reinforcement additives and may efficiently enhance the rheological properties of the nanocomposites. The particle network prevents the nanocomposites from deforming under sustained load, with an additional relaxation process at much longer time scale. Because natural clay and GO are different in cation exchange capacity (CEC), the difference in degree of surface modification also dramatically influences their rheological performance. Cloisite 20A particles that contain 38% alkyl modifier does not influence \( \tau \) as the filler content increases. However, OMGO particles that contain about 45% alkyl modifier make the OMGO/rPBS nanocomposites relax about 100 time slower at a mass fraction of 0.2, as compared to the rPBS matrix.

We made a brief summary to the rest composite systems that we have carried out during this project in chapter 6. Particles employed in these composites possess various geometries, ranging from 0D sphere/cubes, to 1D rods/fibers, and to 2D platelets. We conclude that the surface properties and geometries of the filler particles are playing essential roles to the rheological properties of the nanocomposites. 0D particles only slightly enhance the rPBS matrix even at significantly high filler content. However, for 1D and 2D particles, which possess relatively large aspect ratio, they generally reinforce the rPBS at rather low filler content, due to the formation of particle network.
Samenvatting

Het onderzoeksdoel van dit proefschrift betreft het vanuit de basis ontwerpen van intrinsiek zelf-reparerende polymeer nanocomposieten. In hoofdstuk 1 wordt een inleiding gegeven van zelf-reparerende materialen, met een classificatie van de verschillende mechanismes. In de latere hoofdstukken wordt het viscolelastische gedrag van onze materialen geanalyseerd aan de hand van mechanische netwerk modellen, waarin diverse elementaire mechanische eenheden, zoals veren en dempers, op een aantal verschillende manieren worden samengevoegd. Van de modellen met maximaal drie basiselementen worden de dynamische mechanische ($G(\omega)$) en compliantie ($J(t)$) functies afgeleid.

In hoofdstuk 2 beschrijven we de synthese van polyborosiloxane (PBS), het door ons gebruikte zelf-reparerende supramoleculaire matrix materiaal, aan de hand van een procedure uit de vorige eeuw. We beschrijven van dit reeds bekende materiaal een aantal nieuwe aspecten, die in het verleden onderbelicht zijn gebleven, zoals de reactie kinetiek, de karakterisering van de structuurentwikkeling, de mechanische eigenschappen, de glasovergangstemperatuur et cetera. Het gezuiverde PBS materiaal, met goed gedefinieerde boorzure (B(OH)$_2$) eindgroepen, dat gebruikt wordt voor verder onderzoek, noemen we rPBS.

In hoofdstuk 3, worden de intermoleculaire interacties die optreden in PBS, en die aanleiding geven tot het zelfherstellende vermogen met moderne technieken onderzocht. Behalve de bekende dynamische netwerk vorming door waterstofbruggen worden ook reversibele covalente boroxaan (B–O–B) bindingen gevormd. Bij kamertemperatuur condities vormen de boroxaan stucturen bij voorkeur “Boroxine” trimere ringstructuren. Door middel van het vaste- stof MAS $^{11}$B NMR spectrum kan worden vastgesteld dat er bij kamertemperatuur zowel $sp^2$ trigonale en $sp^3$ te-
traedrische B atomen in rPBS aanwezig zijn. Tijdens dehydratatie wordt gevonden dat het aantal boroxaan groepen toeneemt ten koste van de boorzure eindgroepen. De verhouding van sp\(^3\) boor ten opzichte sp\(^2\) boor stijgt eveneens. Onder normale omgevingscondities, kamertemperatuur en relatieve vochtigheid, kunnen de boroxaan groepen weer gehydrolyseerd worden tot boorzure eindgroepen waardoor het supramoleculaire gedrag van rPBS weer hersteld wordt.

Hoofdstukken 4 en 5 beschrijven respectievelijk het versterkende effect van de toevoeging van nanoklei deeltjes (Cloisite 20A) en het flexibele grafeen oxide (GO). Aangezien PBS moleculen voorzien zijn van hydrofiele boorzure eindgroepen leidt de toevoeging van klei en grafeen oxide tot de vorming van zachte nanocomposieten, via interactie met het hydrofiele oppervlak van de toegevoegde nanodeeltjes. De toevoeging van een massafractie van 0.001 GO deeltjes veroorzaakt thixotroop gedrag van het GO/rPBS nanocomposiet. Bij verdere toename van de massafractie GO tot 0.01 ontstaat een laagvisceus thixotroop materiaal. Het oppervlak van natuurlijke nanoklei deeltjes is minder hydrofiel waardoor de viscositeit minder sterk daalt en tevens wordt een gepercoleerd elastisch netwerk van kleideeltjes gevormd. Bij een hoog klei gehalte, met massafractie 0.6, ontstaat een thixotrope pasta. Cloisite 20A en OMGO zijn organisch gemodificeerde nanodeeltjes met dezelfde alkyl modificatie van het oppervlak. Deze gedragen zich initieel als normale vulmiddelen en geven boven de percolatiegrens een verbeterd reologisch gedrag van het PBS nanocomposiet. Het ontstane netwerk voorkomt deformatie van het nanocomposiet onder langdurige belasting en geeft aanleiding tot een additioneel relaxatie mechanisme bij lange tijd. Aangezien GO en natuurlijke klei een ander kation uitwisseling vermogen (CEC) tonen is het verschil in hun reologische gedrag tamelijk groot. Cloisite 20A deeltjes met 38% alkyl modificatie beïnvloeden de waarde nauwelijks bij toenemend gehalte terwijl OMGO deeltjes met ongeveer 45% alkyl modificatie, bij een massafractie van 0.2, de relaxtietijd ongeveer 100x vertragen ten opzichte van de rPBS matrix.

Tenslotte worden in hoofdstuk 6 nog summier andere composiet systemen beschreven die zijn onderzocht. De gebruikte deeltjes hebben verschillende vormen zoals 0D bolletjes/kubusjes, 1D staafjes/vezeltjes en 2D plaatjes. We kunnen vaststellen dat de oppervlakte eigenschappen en de deeltjesvorm van essentieel belang zijn voor de reologie van de gevormde nanocomposieten. De 0D deeltjes hebben
nauwelijks invloed op de reologie van de rPBS matrix, zelfs bij aanzienlijk deeltjesgehalte. Anderzijds geven de 1D en 2D deeltjes door hun grote anisometrie al bij lage gehalten aanleiding tot versterking van de rPBS matrix, wat ongetwijfeld veroorzaakt wordt door het efficiënt kunnen vormen van een gepercoleerd deeltjes netwerk.
Curriculum Vitae

Zhen Liu was born on June 7, 1983 in Harbin, P.R. China. In June 2006, he completed his bachelor in food science and technology, in Henan University of Technology. He enrolled for the master education in September 2006 in biochemical engineering at Delft University of Technology. He obtained his master degree in May 2009. Between June 2009 and October 2010, he worked with Prof. Schmidt-Ott as a researcher. In October 2010, he started working as a PhD candidate under supervision of Prof. S.J. Picken and Dr. N.A.M. Besseling on self-healing polymeric nanocomposites.
Published Work


Acknowledgments

- I would like to acknowledge my supervisors Prof. S.J. Picken and Dr. N.A.M. Besseling. They have not only given me the opportunity to work as a PhD researcher, not only advised me how to professionally think and work.

- I sincerely acknowledge all the technicians in NSM, ASM and OMI. You have been so nice and patient when I make mistakes, been cheerful when I succeed, been critical when I consult you about techniques. You are equally important and respectable as my supervisors.

- I would like to acknowledge Prof. van der Zwaag for initiating such outstanding self-healing projects, and giving me accessibility for using equipments in the group of Novel Aerospace Materials. Dr. M. Hegde’s help is essential in the first phase of my PhD.

- I thank my NSM and OMI group members, for creating an enjoyable atmosphere and accompanying me in the first and second halves of my PhD. I acknowledge my colleague Wouter Hendriksen and Hanan Al-Kutubi for correcting my dutch propositions. I thank the great effort of Prof. Picken, Duco Bosma and Bart Boshuizen for editing the dutch summary for me.

- I thank my wife and worship her. She has brought our family a son and a daughter, as well as a Doctor of 12 journal publications.