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ARTICLE

Synthesis of polyborosiloxane and its reversible physical cross-links

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A hybrid polyborosiloxane was synthesized, and whereafter the effect of boron concentration on the Si-O:B weak-bonding of polyborosiloxane was investigated mainly by means of FTIR and dynamic rheology. The interaction between boron and oxygen plays an important role on the viscoelastic properties of polyborosiloxane which forming a reversible physical cross-links through temporary Si-O:B weak bonds splitting and rejoining. Dynamic frequency sweeps and dynamic time sweeps showed frequency-dependent elastic modulus, indicating the presence of physical network structure in polyborosiloxane. Elastic modulus slowly decreased with a higher temperature owing to the increased chain segment mobility and decreased strength of physical cross-links. This behavior was believed to be related with the temperature-dependent of Si-O:B weak-bonding as also revealed by FTIR results. Further dynamic mechanical analysis on this behavior showed that elevated temperature tended to increase the motion of chain segment, resulting in less weak-bonding interactions and thereby a weaken network with a lower flat elastic modulus. These results suggest that the reversible physical cross-links can be regarded as an optional simple way to modulate the viscoelastic properties and to tailor the network structure of silicone rubber mixing with polyborosiloxane that can used as resilient rubber in practical applications.

I. Introduction

Organic–inorganic materials offer exceptional opportunities to obtain materials with unique properties such as resistance to low and high temperatures, slow-burning, and high mechanical strength^[1], they often exhibit remarkable thermal, electrical, and gas or water barrier properties^[2, 3]. The properties of hybrid materials are intimately related to both microstructure and structure of network, i.e., the way which organic and inorganic molecules are organized^[4–6]. An important branch of these polymers are polyborosiloxanes (PBS)^[7] which have attracted considerable industrial and academic interest over the past few years.

The polyborosiloxane nicknamed ‘bouncing putty’ which like a slowly flowing viscous liquid is well known because of its fascinating mechanical and viscoelastic properties^[8]. It can exhibit plastic, elastic or rigid mechanical behavior in their dependence on the loading conditions and temperature. In spite of its brittle fracture under a rapid extensional strain, it still reveals significant viscoelasticity, which can be used as

resilient rubber in the research of damping buffer and shock transmission unit^[9–11].

From the viewpoint of practical applications^[12–14], a good understanding of the network structures of polyborosiloxane, on which the properties of end products directly depend, is of paramount importance and worthy of in depth study. In an effort to obtain insight into the effect of temperature and shear stress on the physical network structures of polyborosiloxane, we prepared linear polymethylphenylborosiloxanes (PMPBSs) with different boron content (B/Si molar ratio of 1/300, 1/100, 1/10, 1/5, 1/3) by new synthesized method and tested them under oscillatory shear, concerning rheology properties of which have not been described in the literature so far. An interesting result dealing with the change of systems elasticity with different boron content, temperature, shear stress was discussed. Our work suggests that the viscoelastic properties are concerned with the action of Si-O:B weak-bonding forming a reversible physical cross-links, thus it can be regarded as an optional simple way to modulate the viscoelastic properties and provide reference in practical applications.

II. Experimental section

Materials and sample preparation

The dichlorphenylmethylsilane (MePhSiCl_2) was purchased from Kelong Chemical Co., Ltd. Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) were supplied by Tianjin Bodi Chemical Reagents. All reagents except dichlorphenylmethylsilane were used as received, without further purification.

As known that MePhSiCl_2 obtained by thermal condensation contains trifunctional monomers such as MeSiCl_3 and PhSiCl_3 , more or less illustrated in Fig.1 (a). Of which, the boiling point of MeSiCl_3 (66°C) is low, and easy to be removed by simple fractionation. But as for MePhSiCl_2 (205°C) and PhSiCl_3 (201°C) is very close to each other^[15, 16], using the general fractionation is difficult to separate them efficiently. In order to make the purity of raw material to meet the requirements of hydrolysis, we use physical and chemical purification method to purify methylphenyldichlorosilane. At $-3\sim-12^\circ\text{C}$, PhSiCl_3 is more active to mixed with solution of water and acetonitrile, producing silanol group, thereby increasing the difference in boiling point of MePhSiCl_2 and PhSiCl_3 , finally MePhSiCl_2 with higher purity (93.66%) can be obtained by distillation as shown in Fig.1 (b).

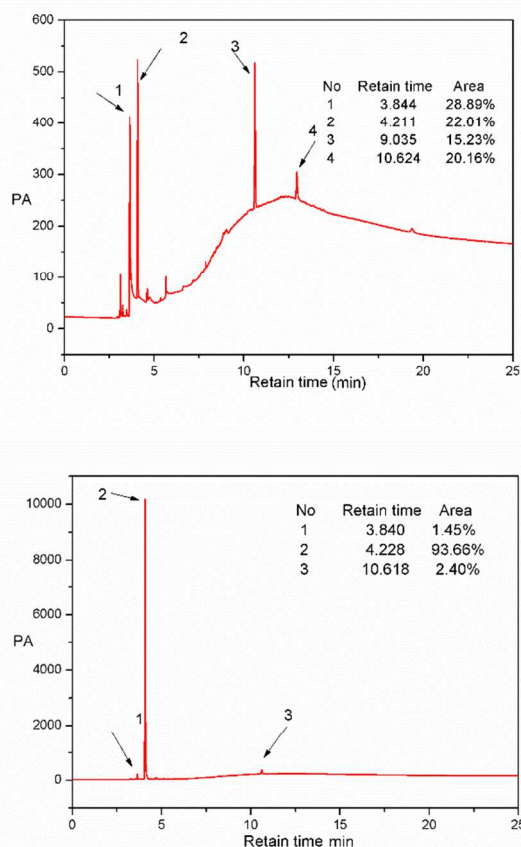


Figure 1 (a) (b) Gas phase chromatography curve of unpurified and purified MePhSiCl_2

The polyborosiloxane were synthesized according to the following procedure: Solutions were prepared at room temperature by stirring the sodium tetraborate with the distilled water for two hours. Then one mol of dichlorphenylmethylsilane was gradually added into the solution under stirring within half an hour. The transparent reaction mixture was kept at room temperature until the precursor sol became viscous.

Poured out the solution and put the precursor in vacuum oven at 80°C for 12 h. The precursor was then heated to 80°C in oil-bath for 40 min. 0.1 mol hydroxyl silicone oil was gradually dropped within half an hour until completely dissolved under stirring. Five sets of solutions with B/Si molar ratio of 1/300, 1/100, 1/10, 1/5, 1/3 labeled as PBS-1 to PBS-5 were prepared (Table.1).

Table 1 Compounding of polyborosiloxane

B:Si	1:300	1:100	1:10	1:5	1:3
Materials	PBS-1	PBS-2	PBS-3	PBS-4	PBS-5
Si-Cl2 (mol)	1	1	1	1	1
$\text{Na}_2\text{B}_4\text{O}_7$ (mol)	0.0009	0.00275	0.0275	0.055	0.09
Solvent(H_2O)(ml)	100	100	100	100	100
Si-OH oil(mol)	0.1	0.1	0.1	0.1	0.1

Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectra were collected with a spectral resolution of 2 cm^{-1} and the wavenumber range was from 500 to 4000 cm^{-1} by the KBr disk method in transmission mode; 32 scans were always accumulated with a Nicolet Magna 560 (Nicol American) infrared analyzer using KBr disks at room temperature.

To confirm the existence and transformation of Si-O-B bonds in mixture, temperature-variable FTIR spectra were collected in situ during the thermal treatment on the Nicolet Magna 560 FTIR spectrometer equipped with a temperature controller. The dynamic spectrum was collected every 5 min until there was no significant spectroscopic change. Using the temperature controller with temperature fluctuation of only $\pm 1^\circ\text{C}$, the transmission mode was applied in the FTIR measurements, and 16 scans were accumulated for a signal averaging with a 2 cm^{-1} resolution to obtain the data with an acceptable signal-to-noise ratio.

Dynamic rheological tests

Dynamic rheological tests, which can offer a more direct correlation with microstructure, were carried out using a rotational rheometer (AR2000EX, TA instruments, USA) with parallel plates (25 mm in diameter). The rheometer is equipped with a Peltier control system that provides accurate control of temperature ($\pm 0.1^\circ\text{C}$). Then, the speed and the force of the compression process to produce an appropriate gap for the dynamic rheological tests were strictly controlled by the rheometer. Moreover, before each dynamic test, a steady pre-shear was applied on the sample to erase the effect of any previous shear history and to ensure that the sample established its equilibrium structure.

Dynamic Mechanical Analysis

The samples were prepared by mixing methylvinylsilicone rubber (VMQ) with polyborosiloxane and the component ratio was controlled in 100:5. The compounds were press cured under 10 MPa at 60°C for 15 min. The tests were performed in an air-circulated oven with temperature fluctuations less than $\pm 1^\circ\text{C}$. The measurements were conducted on a DMA Q800 (TA corporation America) apparatus equipped with liquid nitrogen cooling instrument. The geometry of deformation was tension film model. The tests follow a maximum strain of 0.1% to obtain linear viscoelastic properties. For the temperature sweep spectrum, the temperature range was from -120°C to 90°C with a heating rate of $3^\circ\text{C}/\text{min}$ at the frequency of 1 Hz. Under successive sinusoidal strain $\gamma = \gamma_0 \exp(i\omega t)$, the real and imaginary part of the complex modulus ($E^* = E' + iE''$) were recorded simultaneously.

III. Results and discussion

3.1 Characterization of hybrid polyborosiloxane

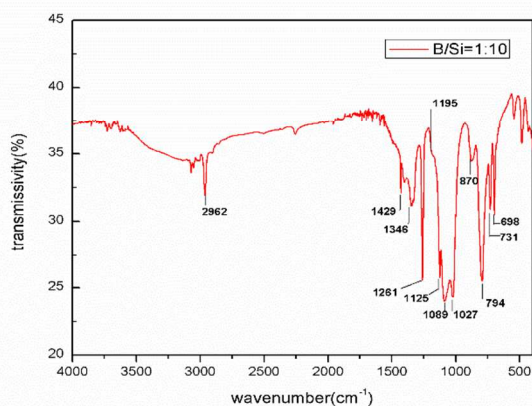


Figure 2 FTIR spectra of polyborosiloxane in the wavenumber range of $4000\text{--}500\text{ cm}^{-1}$

As shown in Figure 2, most representative sample of PBS-3 (B:Si=1:10) will be reported and discussed. The FTIR spectra of the hybrid polyborosiloxane show the following main bands: $\nu\text{B-O}$ in the range $1500\text{--}1300\text{ cm}^{-1}$, $\sigma\text{Si-CH}_3$ in the $1272\text{--}1262\text{ cm}^{-1}$, $\nu\text{Si-CH}_3$ at 794 cm^{-1} , $\nu\text{Si-O}$ at 1089 and 1027 cm^{-1} . The presence of boron gives rise to peaks at $1500\text{--}1300\text{ cm}^{-1}$ ($\nu\text{B-O}$) and at 1195 cm^{-1} ($\sigma\text{B-OH}$). The strong Si-O absorption at 1089 cm^{-1} with a shoulder at 1125 cm^{-1} is characteristic of linear Si-O-Si chains [17, 18]. The band at 870 cm^{-1} and 698 cm^{-1} is the fingerprint of the polyborosiloxane bridges, $=\text{B-O-Si}$. Note that the values are very close to the ones suggested by other researchers [19-24].

Also, the chemical structure of the PBSs was confirmed by $^{29}\text{Si-NMR}$ methods. In the $^{29}\text{Si-NMR}$ spectra (Fig.3) are present signals of silicon atoms of all units present in the structures of these copolymers: a main peak at -21 ppm that can be assigned to $[\text{R}_2\text{SiO}]$ units, and another peak located at -78 ppm corresponding to the unit $[\text{RSiO}_{3/2}]$ environment.

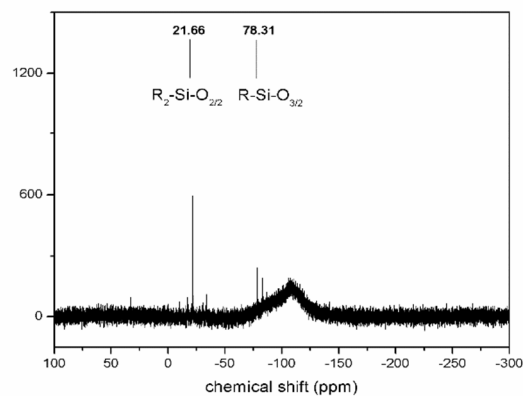


Figure 3 $^{29}\text{Si-NMR}$ spectrum of polyborosiloxane

More detailed analysis [15, 25] indicate that, PBSs may have many sequences of the siloxane chain as shown in figure 4. Their tacticity depends on the stoichiometry of monomers, the presence of different structural units, the steric hindrance at silicon atoms, and the reaction conditions [1, 25].

The formation of the network structure strongly depends on the relative boron amount in respect of the available silanol groups [26, 27]. We used MePhSiCl_2 and $\text{Na}_2\text{B}_4\text{O}_7$ as reactants to reduce the silanol groups and it showed that the presence of polyborosiloxane bonds facilitates the formation of linear structures.

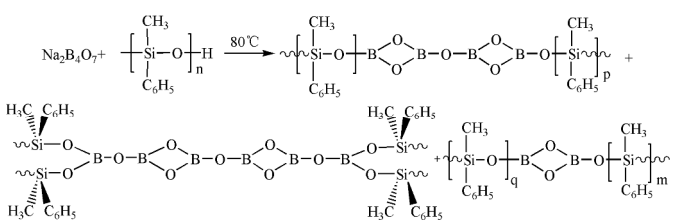


Figure 4 Synthesis mechanism of polyborosiloxane

3.2 Influence of B content and temperature on structures of PBS

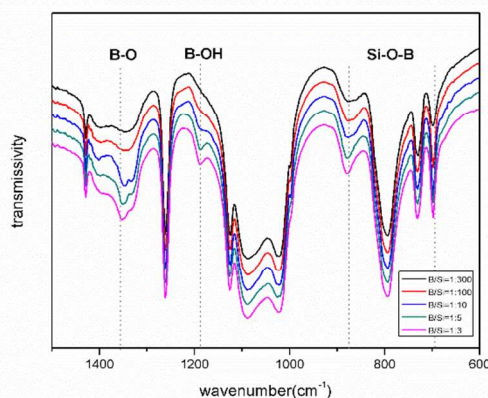


Figure 5 FTIR spectra recorded on the polyborosiloxane with different B/Si molar ratio

To illustrate the effect of the boron load, FTIR recorded on PBS-1 to PBS-5 are shown in Figure 5, where the band appearing at 698cm^{-1} is attributed to deformation strength of the Si-O-B bonds that, together with the band located around 870cm^{-1} evidences the incorporation of boron atoms into the silica network. While for the sample PBS-3 with B/Si=1:10, the two peaks become distinct, suggesting the presence, in this sample, of polyborosiloxane bridges. In the PBS-4 and PBS-5 with higher B content, the bands at 870cm^{-1} and 698cm^{-1} are still present, but their intensity does not increase significantly compared to the PBS-3 sample. On the other hand, by increasing the boron content from B/Si=1:300 to B/Si=1:3, the intensity of the peaks related to the B-O-B and B-OH bonds increases (see bands at $1500\text{-}1300\text{cm}^{-1}$ and at 1195cm^{-1}), suggesting an increase of the total boron load in the sample.

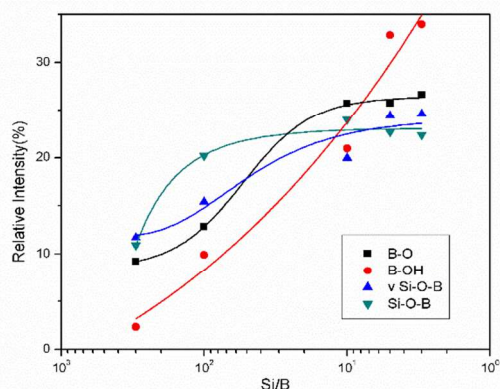


Figure 6 Relative intensity of the bands obtained from deconvolution analysis of the spectra

The evolution of the bands with composition has been followed through deconvolution analysis of the FTIR spectra (Fig.6), in which, the relative intensity of Si-O-B bridges, B-O and B-OH groups shows an increasing tendency when the boron content is increased. These results suggest that the number of polyborosiloxane bridges initially increases, while a plateau is reached when the boron load up to a certain level. Afterwards, any further boron addition does not increase the amount of boron incorporated in the silica network but forms preferentially B-OH and B-O-B bonds.

Meanwhile, the temperature dependent behavior of Si-O-B bands from room temperature to 140°C was monitored by the real time FTIR (Fig.7(a)). The PBS-3 was taken as representative sample. During the heat treatment, the peaks originating from Si-O-B groups at 870cm^{-1} weaken in the samples, while the relative intensity of Si-O-B bridges at 698cm^{-1} is also comparable to that in the same sample. When the temperature elevate to 90°C , the intensity decrease rapidly. Detailed analysis will be shown later in the discussion section, we tentatively consider there are weak-bonding interactions between oxygen and boron in polyborosiloxane, and the interactions are dependent on temperature.

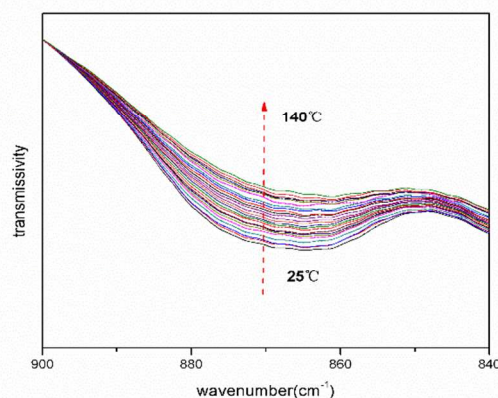
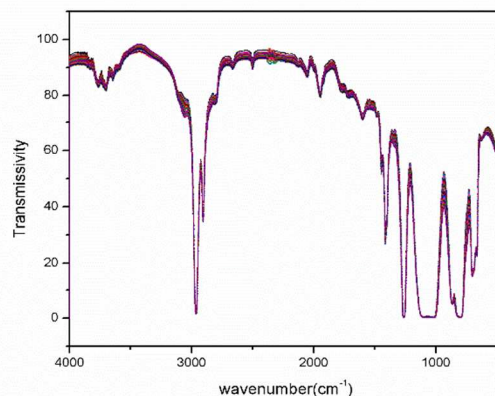


Figure 7 (a) (b) FTIR spectra in the stretching region from 840 to 900cm^{-1} of PBS-3 during thermal treatment

This promising result prompted us to investigate the influence of some application parameters (boron load and temperature) on the incorporation of boron into the silica network.

3.3 Dynamic rheological properties of polyborosiloxane

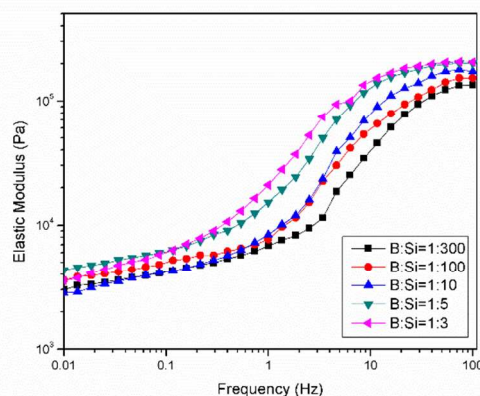


Figure 8 Frequency-dependent behavior for the elastic modulus (G') of the polyborosiloxane

The dynamic frequency spectrum for a given system can provide a signature of the microstructure existing in the system. The dynamic rheological tests were conducted at a strain amplitude of 0.1 %, and test temperature was 60°C. The dynamic modulus (G' , Pa) versus frequency of PBS-1 to PBS-5 are shown in Fig.8. PBS-5 (B/Si molar ratio of 1/3) shows a highly elastic response than other samples at 60°C. This elastic behavior caused us to believe that there are network structures generated by Si-O:B weak-bonding interactions exist in our samples. Owing to the B ions, its weak-bonding interaction is particularly apparent in B-rich samples leading more network structures, wherefore elastic modulus G' enhance under relatively low frequency range and, ultimately, kept at a rather high level.

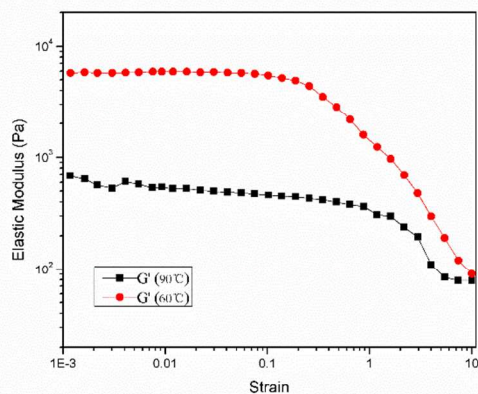


Figure 9 Dependence of the elastic modulus on strain amplitude of polyborosiloxane

In addition to the frequency sweeps, isothermal studies have also been carried out at temperatures between 60°C and 90°C to evaluate the strain stability of the polyborosiloxane. Dynamic strain sweeps for the PBS-1 to PBS-5 at 60°C and 90°C (only shown for the PBS-3 samples for clarity) show in Fig.9.

At 60°C the elastic modulus G' , which characterizes the strength of the network structure, of PBS-3 is almost one orders of magnitude larger with that of 90°C at the same boron content, indicating more Si-O:B weak-bonding interactions lead to a stronger network. Moreover, for the PBS-3, G' at 90°C is lower than that at 60°C under the low strain range, suggesting a weaker network at a higher temperature, which is certainly consistent with observations over the temperature dependent behavior of Si-O-B in Fig.8.

Under shear mode at 60°C, as shown in Fig. 9, the elastic modulus changes little with a plateau when the test strain amplitude is below approx.0.2% indicating that small strain will not change the structure nature of Si-O:B, but decreases obviously by applying larger strain, which means the weak-bonding interaction becomes weaker. However, the situation becomes different at high temperature 90°C, where, after undergoing such shearing step, the elastic modulus continues to slowly drop and collapses to the end with a higher shear force. In order to confirm the interesting temperature behaviors of

PBS and examine whether the change in elastic modulus with temperature is not an occasional phenomenon, we further performed dynamic time sweep at 60°C and 90°C respectively, as shown in Fig.10 in the following sections.

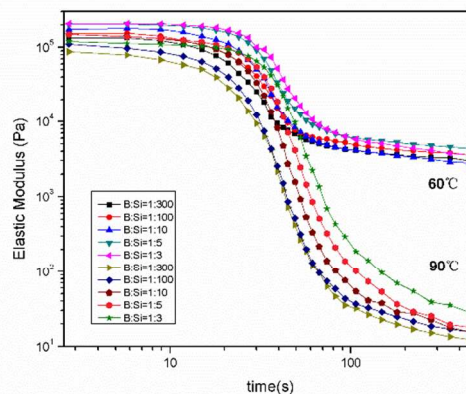


Figure 10 The time sweep for the polyborosiloxane at 60°C and 90°C

The time sweep was conducted at a strain amplitude of 0.1% and a constant frequency of 1 rad/s. This change in the elastic modulus of all PBS samples can be explained by the chain segment mobility and strength of weak-bonding interactions among the B ion and O ion which is in good agreement with the findings for the temperature dependent behavior of Si-O:B band.

It is discussed above that a higher temperature will give a lower elastic modulus for the samples, and the results shown here at 90°C also indicate that boron content makes contribution to the rheological response of higher temperature. Since the role of boron in PBS-1 (B/Si molar ratio of 1/300) has not fully displayed, the fragmentation of this network structure could be more easily induced by the largely increase in the chain segment mobility and the substantially decrease in the strength of weak-bonding interactions with higher temperature, as a consequence the elastic modulus G' reduced to a minimum. It should be pointed out that the elastic modulus of B-rich sample like PBS-5 (B/Si molar ratio of 1/3) is still higher than that of others, because the rest of boron tend to form a new weak-bond with oxygen, which might be droved by the segments movement. The result here strongly suggests that, boron content, the only different condition in this particular case, indeed influences the dynamic rheological properties and thereby the network structure of polyborosiloxane.

By contrast, for the observation at 60°C, G' remained constant at almost the same level after a period of shear time. Though the chain segments mobility was increased and the strength of weak-bonding interactions was decreased as the same time, the network structure fragments were almost kept in their original positions due to the relatively low temperature and as a result, therefore less probabilities to be close to other boron or oxygen to form new weak-band, and finally exhibit with a nearly flat G' .

3.4 Dynamic Mechanical Analysis

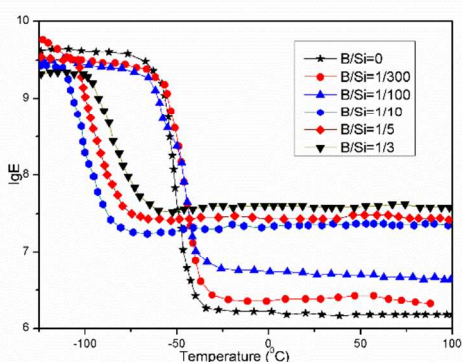


Figure 11 Dynamic mechanical properties of VMQ with different B/Si molar ratio

As shown in Fig.11, the samples of polymethylvinylsiloxane (VMQ) and PBS/VMQ blend were tested by the temperature range was from -120°C to 90°C with a heating rate of $3^{\circ}\text{C}/\text{min}$ at the frequency of 1 rad/s. The storage modulus (E'), curves of samples with different boron content are shown in Fig.11.

As illustrated previously, the chain segment mobility and strength of weak-bonding interactions among B and O are the key factors to intensive change of elastic modulus. For a specific frequency, the storage modulus decreases with increasing deformation from a linear plateau value to a lower value at high amplitude of the deformation, whereas the loss modulus exhibits a pronounced peak.

The long-range connectivity in the filling material may arise from physical interactions instead of from chemical bonds^[31]. On one hand, the regularity of the main chain structures of polymethylvinylsiloxane (VMQ) was been destroyed by the incorporation of polyborosiloxane, as consequence, crystallization of VMQ at low temperature ($-125^{\circ}\text{C}\sim 50^{\circ}\text{C}$) could be suppressed, leading to storage modulus decreased. But in the meantime, the introduction of polyborosiloxane segments enhancing the Si-O:B weak-bonding interactions which substantially reduces the free volume for chain movements will increase the network density of chain of VMQ, therefore, indeed exerts great influence on storage modulus from normal temperature to high temperature. Based on this evidence, we deem that the change in G' with temperature should be mainly related to the different amount of combinative boron, the abridged general view of which has been shown in detail in next section.

On the other hand, for the behavior rules of PBS-1 and PBS-2 with lower B content, is consistent with the change in VMQ (B/Si molar ratio of 0). As we can observe from the curves, high boron content leading more weak-bond, once again, indeed influences the dynamic properties, and thereby increasing energy dissipation between the molecular chains and improving damping properties of polysiloxane, manifesting

that the properties are governed by the physical crosslinking nature of the main chain.

3.5 Si-O:B weak-bonding interaction

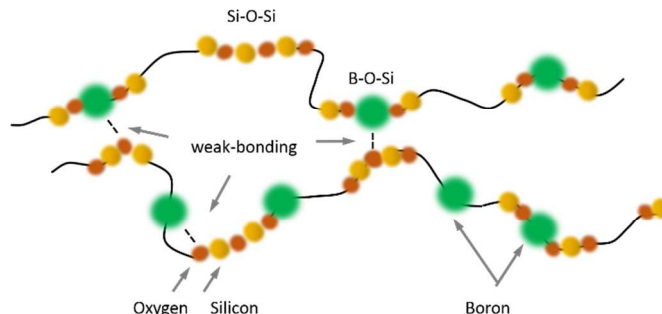
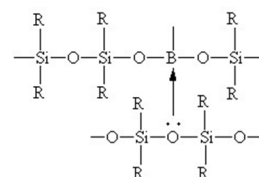


Figure 12 Abridged general view of weak-bonding crosslink

Since the electronegativity of B (~ 2.0) is significantly smaller than that of O (~ 3.5) and the outer electron configuration of B is $1s^2 2s^2 2p^1$, which can be coordinatively unsaturated with sp^3 hybrid orbitals. The occupation of electrons on the B 2p orbitals is expected to be not significant, then can accept an unshared-electron pair of the oxygen from the silicone backbone^[28-31], which is formed weak-bonding interaction between adjacent molecules (electron bridge), causing physical cross-links through temporary B-O dative bonds splitting and rejoining due to thermal fluctuations^[8], the physical cross-links is reversible and schematic plot as shown:



According to the different amount of combinative boron, the polymer can obtain certain special nature which cannot be obtained from crosslinking by primary valence bond and an alkylene bridge or siloxane bridge.

Weak-bonding physical crosslink is formed, as shown in Fig.12. Analysis of the infrared spectra can demonstrate the presence of cooperative bonding between B and O. As shown in Fig.7 (b), since Si-O-B produces a remarkable absorption peak around 870cm^{-1} and the shift of the peak to lower wavenumber is related to the existence of the weak-bonding, the peaks at 870cm^{-1} for the PBS sample confirm the existence of the Si-O:B weak-bonding. Obviously compared with the peak at 870cm^{-1} , the peak at 868cm^{-1} becomes wider and its intensity is weakened, implying that the weak-bonding interaction in the sample within the heating step is not stronger than before, and thereby less physical crosslinking exist in the sample after the thermal treatment.

The same dynamic strain sweeps at 60°C and 90°C were conducted on the PBS with the different boron concentration, 1/300, 1/100, 1/10, 1/5, 1/3, respectively (Fig.9). For all the

concentrations, the elastic modulus (G') remains almost constant under the small strain and decreases after a long shear time with larger strain. The values of G' at two different temperatures during the time sweeps were collected and summarized in Fig.10. For each temperature, the elastic modulus decreases with boron concentration following the above rules observed from dynamic strain sweeps.

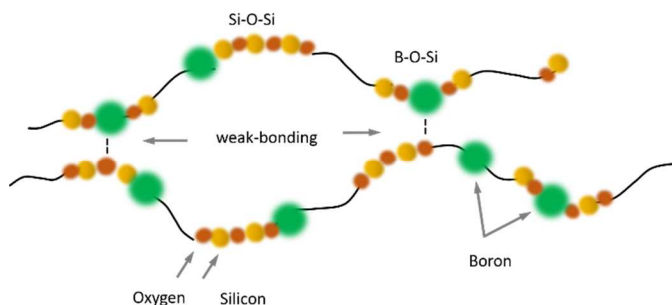


Figure 13 Abridged general view of weak-bonding under small shear force or low temperature

Consequently, it is considered that the small shearing force makes the weak-bonding structure of Si-O:B become constantly dissociate and part of structure fragments regain under lower temperature, and finally forms a less stronger network structure with a lower G' than before. Though the chain segments mobility was increased and the strength of weak-bonding interactions was decreased as the same time as is shown in Fig.13, the physical crosslink fragments were almost kept in their original positions due to the relatively low temperature or small shearing force and as a result, less probabilities to come near to other B or O finally exhibit with a nearly flat G' .

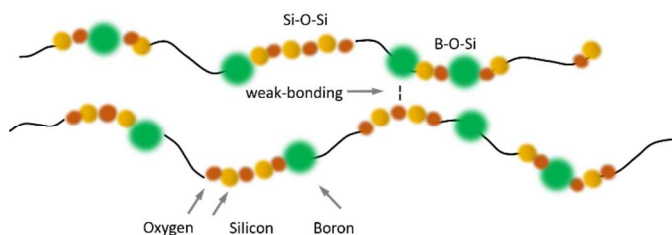


Figure 14 Abridged general view of weak-bonding under large shear force or high temperature

By the contrast analysis, under the effect of larger external shear forces or higher temperature, the disaggregation of this network structure could be more easily induced by the largely increase in the chain segment mobility and the substantially decrease in the strength of weak-bonding interactions. As is illustrated in Fig.14, the segments movement drives the rest of B to form a new weak-bond with O, but the elastic modulus fall far below its initial value as being reflected by dynamic time sweeps.

Furthermore, the result here in this particular case suggests that, boron content, the only different condition become a dominant factor to the change tendency of elastic modulus. That is, owing to the boron, weak-bonding interaction is particularly apparent

in B-rich samples leading more network structures by physical crosslink to present, whereby leads to elastic modulus G' enhance and, ultimately, kept at a relative high level for such reasons.

IV. Conclusions

PBS-1 (B/Si=1/300) to PBS-5 (B/S=1/3) were prepared (using sodium tetraborate and bifunctional silane,) and afterwards the dynamic rheological measurements were performed to investigate the effect of boron concentration on Si-O:B weak-bonding.

The frequency-dependent behavior for the elastic modulus (G') is observed, indicating the presence of a network structure by Si-O:B weak-bonding physical crosslink in all samples. The nature characteristic of boron and oxygen plays an important role on the temperature-dependent behavior of PBS as revealed by dynamic time sweep experiments (at a strain amplitude of 0.1% and a constant frequency of 1rad/s), indeed influences the dynamic rheological properties and thereby the network structure of polyborosiloxane.

It is found that a higher temperature will give a lower elastic modulus for the samples, because the fragmentation of physical crosslink could be more easily induced by the largely increase in the chain segment mobility and result in the substantially decrease in the strength of weak-bonding interactions, as a consequence the elastic modulus G' reduced. This behavior was believed to be related with the temperature-dependent of Si-O:B weak-bonding as also revealed by FTIR results. From the observation at lower temperature, G' remained constant at almost the same level after a period of shear time. The weak-bonding structure of Si-O:B constantly dissociate and part of the fragments regain under lower temperature, and hence there is less chance to approach to other B or O finally forms a less stronger network structure with a lower G' than before. These results suggest that the reversible physical cross-links can be regarded as an alternative, simple way to modulate the viscoelastic properties, and in turn tailor the network structure of silane rubber mixing with polyborosiloxane.

Notes and references

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