Role of Interface Structure and Chain Dynamics on Diverging Glass Transition Behaviour of SSBR-SiO$_2$-PIL Elastomers

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Mixing Procedure: The whole mixing process of preparing SSBR-SiO$_2$ composites was divided into three stages. First, the chamber temperature of the internal mixer and the rotor speed was set to 50 °C and 50 rpm respectively. Then, SSBR and PBD were added into the internal mixer at 60 °C for plasticizing. After a certain time of mixing, SiO$_2$ was added into the chamber and blended with the polymers followed by the addition of PIL and TESPT into the chamber. After 2 min, stearic acid and paraffin were added to the SSBR-SiO$_2$ mixture. After this stage, the SSBR-SiO$_2$ mixture was cooled to room temperature. In the second stage ZnO, 6PPD and antioxidant (TMQ) were put into the chamber and kneaded for another 5 min. Subsequently, SSBR-SiO$_2$ mixture was again cooled to room temperature followed by successive addition of an accelerator and a curing agent. After uniform mixing, the composite was vulcanized at 150 °C for optimum curing time ($T_{90}$) to form the SSBR-SiO$_2$ polymer composites.

Table S1: HN parameters related to the fit functions shown in Figure 1 (b and c)

| Sample              | $\Delta\varepsilon$ | $\alpha$ (assym) | $\alpha$ (sym) | $\tau_{HN}$ | $\Delta\varepsilon'$ | $\alpha$ (assym) | $\alpha$ (sym) | $\tau_{HN}$ |
|---------------------|----------------------|-------------------|----------------|-------------|-----------------------|-------------------|----------------|-------------|
| SSBR/TESPT          | 1.12                 | 0.65              | 1              | $1.59 \times 10^{-7}$ | 0.41                  | 0.33              | 1              | $5.03 \times 10^{-4}$ |
| SSBR/TESPT-PIL 1.5  | 1.57                 | 0.68              | 1              | $1.26 \times 10^{-7}$ | 0.52                  | 0.39              | 1              | $3.99 \times 10^{-3}$ |

Filler Networking and Mechanical behaviour of SSBR-SiO$_2$ Composites: The storage modulus ($G'$) of the SSBR-SiO$_2$ composites in the rubbery state can reveal the extent of SiO$_2$-SiO$_2$ interactions. Notably, the $G'$ values for all the composites decreases rapidly with increasing strain when the strain amplitude is larger than 1% owing to the ‘Payne effect’. This phenomenon is mainly caused by the deformation-induced changes in the filler-filler network and release of the trapped polymer upon the application of oscillatory shear. Therefore, the change in magnitude ($\Delta G'$) between $G'_0$ and $G'$ at larger strain can be attributed to microstructure changes of the SSBR-SiO$_2$ composites induced by deformation. Consequently, weaker the Payne effect ($\Delta G'$), the better the dispersion of the filler in the polymer matrix. The Payne effects of SSBR-SiO$_2$ composites is depicted in Figure S1 (a) SI. The SSBR/TESPT composite has a more significant $\Delta G'$ (Payne effect) than PIL incorporated SSBR-SiO$_2$ composites. Further the value of $\Delta G'$ consistently decreased with increasing PIL loading indicating a more homogeneous dispersion of filler in the rubber matrix. The chemical interface formed by PIL with its long aliphatic hydrocarbon chain among the SiO$_2$ particles served as a buffer to prevent the neighbouring particles from approaching each other. Additionally, the synergistic combination of TESPT establishes a “molecular bridge” between SiO$_2$ and polymer matrix thereby further weakens.
the direct SiO$_2$-SiO$_2$ interactions, ultimately resulting in a fine dispersion of SiO$_2$ in the SSBR matrix. The mechanical behavior of SSBR-SiO$_2$ composites were characterized by the tensile test; the representative stress-strain curves are depicted in Figure S1 (b) SI and the related mechanical data are collected in Table S2. As illustrated in Figure S1 (b), the mechanical properties of PIL loaded SSBR-SiO$_2$ composites are superior to those of SSBR/TESPT composite. It is of interest to note that the Young’s modulus (modulus at 300%), tensile strength and the elongation at break significantly improved. For instance, the Young’s modulus, tensile strength and elongation at break are increased from 15, 17.3 and 290 for SSBR/TESPT composite to 18, 19 MPa and 303 % respectively, when 1.5 phr PIL was added.

Table S2: Mechanical properties of SSBR-SiO$_2$ composites

| Samples              | 100 Modulus (MPa) | 300 Modulus (MPa) | Tensile Strength (MPa) | Elongation at Break (%) | Toughness (Joules) |
|----------------------|-------------------|-------------------|------------------------|-------------------------|-------------------|
| SSBR/TESPT           | 3.31 (0.5)        | 16.85 (0.3)       | 17.3 (0.4)             | 290 (5.2)               | 7.44 (0.8)        |
| SSBR/TESPT- PIL1     | 3.60 (0.3)        | 15.41 (0.6)       | 17.8 (0.2)             | 293 (6.1)               | 7.24 (0.6)        |
| SSBR/TESPT-PIL1.5    | 3.52 (0.2)        | 18.11 (0.4)       | 19.04 (0.5)            | 311 (4.8)               | 8.08 (0.3)        |
| SSBR/TESPT-PIL2      | 3.75 (0.2)        | 18.97 (0.3)       | 19.62 (0.6)            | 303 (5.4)               | 8.26 (0.4)        |
| SSBR/TESPT-PIL2.5    | 3.64 (0.5)        | 17.82 (0.5)       | 16.52 (0.3)            | 277 (5.7)               | 6.50 (0.2)        |

* the standard error is presented in brackets

Such a simultaneous enhancement of mechanical strength and elongation at break for polymeric composite material is a difficult task. This phenomenon originated from the strong H-bonding and electrostatic interactions between the
surface silanol groups and the PIL. Meanwhile, the H-bonds translate the shear forces during mechanical mixing, which reduces the size of SiO$_2$ aggregates and results in improved filler dispersion$^4$. Further, the chemical interface between SiO$_2$ NPs and PIL reduces the stress-concentrated regions thereby improving the reinforcing efficiency. Hence, the chemical coupling between SiO$_2$ and SSBR chains by TESPT act synergistically to improve the mechanical performance of the composites.

**Figure S2**: Tan δ vs temperature plot for SSBR-SiO$_2$ composites in presence and absence of TESPT unequivocally proving that activation occurs via synergistic combination of TESPT and PIL.
Vulcanization Behavior of SSBR-SiO$_2$ Composites: Curing is essential to transform soft viscous elastomer materials into hard useful engineering products. Therefore, vulcanization process and the processing characteristics of elastomers were followed from the rheometer curves in Figure S4. The curves display the relationship between the resistance of the material (torque) to applied shear and the curing time, thus offering a rather complete depiction of the overall cross-linking kinetics. Relevant parameters deduced from the curing curves are summarized in Table S3. A long marching cure is noticed for SSBR/TESPT without PIL. The delayed vulcanization is associated with
adsorption of the curing agents onto the acidic surface silanol groups on the silica surface that are only partially shielded by TESPT. It is obvious that with increasing PIL concentration, the minimum torque (ML) is significantly reduced which arises from the restrained SiO₂ network and effectively decreases the actual filler volume and may be responsible for the phenomenon. The scorching time (Tₛ₂) is consistently decreased with increasing PIL incorporation, whereas, the maximum torque (Tₘₐₓ), however, took a maximum value and then obviously decreased and remained constant. Several possible reasons can be proposed. First, the H-bonding and electrostatic interactions between SiO₂ and PIL converts the surface silanol groups into silanolate ions and thereby suppresses the adsorption of accelerators onto the silica surface, ultimately increasing their concentration. Second, the phosphonium cation may also accelerate the curing rate by acting as a secondary accelerator. Accordingly, the optimum cure times (T-90) of PIL loaded SSBR composites are much lower than that of the composite without PIL. ML and MH are correlated with the shear modulus of the uncured composites and vulcanizates respectively, that are mainly determined by the filler-filler network, polymer network, and polymer-filler interactions. The difference between these parameters for PIL incorporated composites show a significant increase compared to SSBR/TESPT composite indicating PIL to have reduced the filler-filler networking to a great extent, simultaneously improving the polymer-filler interactions.

**Figure S4:** Vulcanization curves for SSBR-SiO₂ composites with various loadings of PIL in phr.

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Table S3: Curing Parameters of the SSBR-SiO$_2$ composites.

| Samples                | Initial (Lb-in) | ML (Lb-in) | T2 (min) | MH (Lb-in) | T-90 (min) |
|------------------------|----------------|------------|----------|------------|------------|
| SSBR/TESPT             | 5.60           | 5.09       | 1.46     | 25.50      | 6.33       |
| SSBR/TESPT-PIL1        | 5.66           | 4.53       | 1.08     | 26.49      | 4.20       |
| SSBR/TESPT-PIL1.5      | 5.11           | 4.05       | 1.00     | 25.78      | 4.05       |
| SSBR/TESPT-PIL2        | 4.68           | 3.66       | 0.85     | 24.55      | 3.82       |
| SSBR/TESPT-PIL2.5      | 4.43           | 3.18       | 0.76     | 23.84      | 3.43       |

Diphenyl guanidine (DPG), generally used as a secondary accelerator in vulcanization process and has been reported to act as a catalyst for silanization reaction in silica-reinforced polymer composites $^9$. However, DPG decomposes during mixing and vulcanization and releases extremely toxic aniline, which is a major safety concern. The U.S. Environmental Protection Agency (2000) has reported aniline to be a probable carcinogen for humans$^{10}$. Therefore, replacements for DPG are required to improve a safe working environment. Since ionic liquids (ILs) have been reported to accelerate the curing rate of the rubber composites by acting as a secondary accelerator, the vulcanization behavior of the composites was investigated in presence of 1.5 phr PIL and by eliminating DPG completely as shown in Figure S5. Interestingly, the curing parameters of the composite without DPG and with 1.5 phr PIL is improved. The optimum cure times (T$_{90}$) of SSBR/TESPT-PIL1.5 composite is much lower than that of SSBR/TESPT composite. Thus, a slight content of PIL has accelerated the vulcanization due to enhanced interfacial

Figure S5: Vulcanization curves for SSBR-SiO$_2$ composites in presence and absence of DPG.
interaction between silica and SSBR by modification of filler surface and the promoted silanization reaction between silica and TESPT, resulting in more efficient crosslinking of SSBR chains. The difference between maximum torque and minimum torque (MH-ML) for SSBR/TESPT-PIL1.5 composite shows a significant increase than SSBR/TESPT composite due to reduced filler networking and improved polymer-filler interaction, as listed in Table S4. Overall, PIL showed the highest potential to be used as an alternative for DPG in SiO₂/TESPT-reinforced SSBR composites;

**Table S4:** Curing Parameters of the SSBR-SiO₂ composites in presence and absence of DPG.

| Sample               | Initial (Lb-in) | ML (Lb-in) | T2 (min) | MH (Lb-in) | T-90 (min) |
|----------------------|-----------------|------------|----------|------------|------------|
| SSBR/TESPT-DPG       | 5.60            | 5.09       | 1.46     | 25.91      | 6.33       |
| SSBR/TESPT-PIL1.5-   | 6.02            | 4.28       | 1.07     | 27.22      | 4.43       |
| No DPG               |                 |            |          |            |            |

**Dynamic-mechanical Performance of SSBR-SiO₂ Composites:** SiO₂-reinforced SSBR tread composites are extensively used in the tire industry. Therefore, an ideal tread composite must offer improved dynamic-mechanical properties. Specifically, tire tread composites with high loss tangents at lower temperatures exhibit good wet skid performance with highly efficient energy dissipation during automobile braking. Interestingly, the SSBR/TESPT/1.5PIL composite exhibited good wet skid resistance (higher tan δ at 0 °C) as well as higher winter and ice traction (higher tan δ at -20 and -10 °C) compared to SSBR/TESPT as shown in Table S5. The rolling resistance (RR) can be well reflected by the hysteresis of the composites, usually predicted by Tan δ at 60 °C. The lower the Tan δ value, the lower the predicted rolling resistance. As shown in the inset of Figure S6 (a) the loss factor at 0 (wet skid resistance) and 60 °C (rolling resistance) for SSBR/TESPT/1.5PIL composites are increased to 0.231 and decreased to 0.083, compared to 0.187 and 0.105 for SSBR/TESPT composites. Thus, the SSBR/TESPT-PIL 1.5 composite exhibits 20% lower RR compared to SSBR/TESPT composite. By that it means that the viscoelastic energy loss of the tire tread compound prepared from SSBR/TESPT-PIL 1.5 is significantly lower than that of SSBR/TESPT composite. Consequently, the fuel consumption and CO₂ emissions will be significantly lower in SSBR/TESPT-PIL composites. Accordingly, as a proof of concept, the conversion of mechanical energy to heat was studied by measuring the heat build-up of the composites under repeated deformation. The mutual friction among all components of the composite is directly related to the value of HBU. Figure S6 (b) depicts the HBU values of the composite materials.
filled with varying phr levels of PIL. Among these composites, the SSBR/TESPT/1.5PIL composite exhibits the lowest HBU (18.5) owing to the weakest mutual friction among all components due to improved bonding and non-bonding interactions at the polymer-filler interface. However, the heat build-up of SSBR/TESPT is significantly increased (23.1). In SSBR/TESPT composite the breakage and re-formation of the filler network causes internal friction among SiO$_2$ particles, resulting in numerous energy dissipation which might be due to low reactivity between SiO$_2$ particles and TESPT in the absence of PIL. Therefore, considering the overall performance in terms of wet grip, traction and 20% lower RR, the SSBR/TEST-PIL 1.5 composite shows an attractive choice of this elastomer for high performance tire applications.

Figure S6: (a) Comparison of dynamical properties of 2 composites in presence and absence of PIL. (b) Heat build-up of SSBR-SiO$_2$ composites with varying content of PIL in phr.

Table S5: Dynamic Mechanical Properties of the SSBR-SiO$_2$ Composites with and without PIL.

| Properties                     | Sample           | SSBR/TESPT | SSBR/TESPT-PIL1.5 |
|--------------------------------|------------------|------------|-------------------|
| Winter traction (Tan δ @ -20 °C) | 0.311            | 0.484      |
| Ice traction (Tan δ @ -10 °C)   | 0.233            | 0.341      |
| Wet skid resistance (Tan δ @ 0 °C) | 0.187          | 0.231      |
| Rolling resistance (Tan δ @ 60 °C) | 0.105           | 0.0835     |
| Heat build-up (°C)              | 23.1             | 18.5       |
| T$_g$ (°C)                      | -37.6            | -27.6      |
| Rebound resilience @ 60 °C      | 63               | 68         |
References:

(1) Payne, A. R. The Dynamic Properties of Carbon Black-Loaded Natural Rubber Vulcanizates. *Part I. J. Appl. Polym. Sci.* 1962, 6, 57.

(2) Ramier, J.; Gauthier, C.; Chazeau, L.; Stelandre, L.; Guy, L. Payne effect in silica-filled styrene-butadiene rubber: Influence of surface treatment. *J. Polym. Sci., Part B: Polym. Phys.* 2007, 45, 286-298.

(3) Chen, Y.; Li, Z.; Wen, S.; Yang, Q.; Zhang, L.; Zhong, C.; Liu, L. Molecular simulation study of role of polymerparticle interactions in the strain-dependent viscoelasticity of elastomers (Payne effect). *J. Chem. Phys.* 2014, 141, 104901.

(4) Godard, P.; Bomal, Y.; Biebuyck, J. J. Influence of interactions on the tensile behaviour of polystyrene filled with calcium carbonate *J. Mater. Sci.* 1993, 28, 6605-6610.

(5) Lei, Y.; Tang, Z.; Zhu, L.; Guo, B.; Jia, D. Functional thiol ionic liquids as novel interfacial modifiers in SBR/HNTs composites. *Polymer* 2011, 52, 1337-1344.

(6) Lei, Y.; Tang, Z.; Guo, B.; Jia, D. SBR/silica composites modified by a polymerizable protic ionic liquid. *Polymer Journal* 2010, 42, 555-561.

(7) Maciejewksa, M.; Zaborski, M. Ionic liquids as coagents for sulfur vulcanization of butadiene-styrene elastomer filled with carbon black. *Polymer Bulletin* 2018, 75, 4499-4514.

(8) Formela, K.; Wąsowicz, D.; Formela, M.; Hejna, A.; Haponiuk, J. Curing characteristics, mechanical and thermal properties of reclaimed ground tire rubber cured with various vulcanizing systems. *Iran Polym J* 2015, 24, 289-297.

(9) Hayichelaeh, C.; Reuvekamp, L. A. E. M.; Dierkes, W. K.; Blume, A.; Noordermeer, J. W. M.; Sahakaro, K. Reinforcement of Natural Rubber by Silica/Silane In Dependence of Different Amine Types. *Rubber Chem. Technol* 2017, 90, 651-666.

(10) Agency for Toxic Substances and Disease Registry. 2002. Aniline. http://www.atsdr.cdc.gov/toxfaqs/tfacts171.pdf. Accessed May 23, 2014.

(11) Hall, D. E.; Moreland, J. C. Fundamentals of Rolling Resistance. *Rubber Chem. Technol.* 2001, 74, 525-539.

(12) Holmberg, K.; Andersson, P.; Erdemir, A. Global energy consumption due to friction in passenger cars. *Tribology International* 2012, 47, 221-234.

(13) Lei, W.; Zhou, X.; Russell, T. P.; Hua, K.-c.; Yang, X.; Qiao, H.; Wang, W.; Li, F.; Wang, R.; Zhang, L. High performance bio-based elastomers: energy efficient and sustainable materials for tires. *J.Mater. Chem. A* 2016, 4, 13058-13062.

(14) Veiga, V. D. A.; Rossignol, T. M.; Crespo, J. d. S.; Carli, L. N. Tire tread compounds with reduced rolling resistance and improved wet grip. *J. Appl. Polym. Sci* 2017, 134, 45334.

(15) Medalia, A. I. Heat Generation in Elastomer Compounds: Causes and Effects. *Rubber Chem. Technol* 1991, 64, 481-492.