Surface Energy Mapping of Modified Silica Using IGC Technique at Finite Dilution

Yen Wan Ngeow, Daryl R. Williams, Andrew V. Chapman, and Jerry Y. Y. Heng

ABSTRACT: The reinforcing silica filler, which can be more than 40% of an elastomer composite, plays a key role to achieve the desired mechanical properties in elastomer vulcanizates. However, the highly hydrophilic nature of silica surface causes silica particle aggregation. It remained a challenge for many tire manufacturers when using silica-filled elastomer compounds. Here, the silica surface energy changes when the surface is modified with coupling or noncoupling silanes; coupling silanes can covalently bond the silica to the elastomers. The surface energy of silica was determined using inverse gas chromatography (IGC) at finite dilution (FD-IGC) and found to be reduced by up to 50% when the silica surface was silanized. The spatial distribution of silica aggregates within the tire matrix is determined by transmission electron microscopy (TEM) and a direct correlation between aggregate size (silica microdispersion) and work of cohesion from IGC is reported, highlighting surface energy and work of cohesion being excellent indicators of the degree of dispersion of silica aggregates.

1. INTRODUCTION

With an implicit reference to tire applications, most elastomers require rigid particle reinforcement to improve the abrasion and tear performance of the vulcanized elastomer compound. A large variety of mineral particles, also known as fillers, can be compounded with the elastomers, but only a number of fillers provide good reinforcing effects. The commonly used fillers for tire tread applications are carbon black and silica. However, the highly hydrophilic nature of silica surface causes silica particle aggregation. These particle aggregates generally range from 100 to 500 nm. It remained a challenge for many tire manufacturers when using silica-filled elastomer compounds. In 1992, reinforcement using a highly dispersible silica compound, together with the use of solution styrene-butadiene rubber (sSBR) in the SBR/BR (styrene-butadiene rubber/butadiene rubber) blend. The advantages of the silica-silane system are reducing rolling resistance, good wet grip, and comparable wear resistance of passenger car tires compared with a conventional carbon black tire tread compound. The inelastic filler–filler aggregates or agglomerates are significant when the filler is not well dispersed in the elastomer phase. These aggregated filler particles can trap part of the elastomer, which is termed as the “occluded” elastomer. The parameters of the fillers that play an important role for elastomer reinforcement are the particle size, structure, and surface activity. The particle size and the specific surface area of the particle can be related to the interfacial area between the particle surface and the elastomer chains. The filler structures can be related to the degree of irregularity of the aggregation development of the primary particles, and these aggregated primary particles can trap part of the elastomers, affecting the compound properties. It increases the effective filler volume and affects the compound properties, such as the viscosity and modulus of the filled elastomer.

Both of the above parameters will not bring significant effects without the involvement of the third parameter, the surface chemistry or the surface activity of the filler particles. This parameter is responsible for the relative strength of filler–filler interactions, filler–elastomer interactions, and filler interaction with other ingredients during compounding. The energetic heterogeneity and the surface geometric heterogeneity of the particle surface, which have a close association with each other, influence the reinforcement of the elastomer. Surface interactions play a critical role in determining the magnitude of the shift in glass transition temperature, $T_g$, in a layer of the elastomer bound to the surface.
and have been shown to improve the dynamic mechanical performance for the filled elastomer.\textsuperscript{16,25} A broad spectrum of adsorption sites on the particle surface will eventually have an effect on the bonding configurations,\textsuperscript{29} and the heterogeneity sites on the particles can be reduced by pretreatment with heat or surface chemistry modification.\textsuperscript{30} For silica, the adsorption sites are primarily on silanol groups (\textendash SiOH).\textsuperscript{31} A Boltzmann distribution statistical approach has been used in the inverse gas chromatography (IGC) study to understand the convolution of the adsorption sites corresponding to the energetic threshold value.\textsuperscript{32}

Other authors have investigated the surface modification of silica with different silanes during elastomer vulcanization to improve the reinforcement of the elastomer.\textsuperscript{23,33\textendash 40} Silica silanization with bis[3-(triethoxysilyl)propyl]tetrasulhide (TESPT) was compared using thermogravimetric analysis combined with IR detection (TGA-IR) and inverse gas chromatography (IGC) with reaction times varying from 10 min to 24 h. Through TGA-IR analysis, silica silanization with TESPT is largely completed after only 10 min. The silane grafting efficiencies were mainly in the range of 52\textendash 72%. The results also indicated that the 1 h reaction time used in the current study would be sufficient for all of the silanes investigated.\textsuperscript{41}

2. RESULTS AND DISCUSSION

2.1. Dispersive Surface Energy Profiles. The values for the dispersive surface energy component of the untreated and silanized silicas are presented as a function of surface coverage in Figure 1, \( n/n_m \), where \( n \) is the amount of the adsorbate adsorbed and \( n_m \) is the monolayer capacity of the silica particles. S1 is untreated silica, S2\textendash S8 are silicas silanized with coupling silanes, and S9\textendash S12 are silicas silanized with noncoupling silanes. The profiles of Figure 1a,b show that the surface energy values change as a function of surface coverage. This indicates that the samples are energetically heterogeneous, especially the untreated silica (S1), but samples S6 (3-di-(tridecylxypenta-
interaction between the probe molecules as the surface coverage of the same silica. The higher $\gamma^d$ related to the concentration of high-energy sites for the highest energetic sites occupy approximately 0.2% of the silica surface. Figure 2 illustrates how the DTSPM may be attached to the silica surface. The polyether side chains from DTSPM can interact with the silanol groups or water molecules on the silica surface through hydrogen bonds.34

The silicas silanized with TESPT (S2 and S3) exhibit similar $\gamma^d$ profiles, even though the TESPT loadings differ by 4% w/w silica. Silanized silica S5 (bis[3-(triethoxysilyl)propyl]disulfide (TESPD)), with a similar chemical structure to TESPT except having a shorter sulfur bridge, exhibits a similar $\gamma^d$ profile to S2 and S3. As a comparison, the $\gamma^d$ values are close to those observed by Wang and Wolff in their investigation of silica silanized with bis[3-(trimethoxysilyl)propyl]tetrasulfide.39 They reported that the surface energy of silica silanized was greatly reduced.39 The silicas silanized with DTSPM and TESPO, containing long alkyl functional groups, exhibit the lowest and most homogenized $\gamma^d$ profiles, presumably due to their greater surface coverage. Wang and Wolff also reported that the surface energy heterogeneity of modified silica was drastically reduced particularly for octadecytrimethoxysilane.39

For the silicas silanized with noncoupling silanes, similar $\gamma^d$ profiles are observed apart from S9 (octyltriethoxysilane (OTES)), which exhibits a higher profile, possibly arising from incomplete silanization.33 Silica silanized with methyltrimethoxysilane (MTMS) (S10) and trimethylchlorosilane (TMCS) (S12) showed similar $\gamma^d$ across most surface coverages measured, even though TMCS has higher reactivity compared to the rest of the coupling and noncoupling silanes. S11 (methyltriethoxysilane (MTES)) showed the lowest $\gamma^d$ for surface coverages below 0.4%.

Values for $\gamma^d$ at infinite dilution have been reported previously for silica silanized with TESP,30 TESPO,31 TESPD,33 and OTES.53 Taking into account the different IGC conditions used and that a different silica was used with TESP and OTES, the values reported are in good accord with the surface energies observed in Figure 1a,b when zero surface coverage is approached.

2.2. Specific Surface Energy Analysis. The surface properties of the silica also include the specific interactions resulting from the presence of polar functional groups on the surface, such as hydroxyl groups. The specific (acid–base) surface energy profiles are obtained by using a monopolar acidic probe (dichloromethane) and a monopolar basic probe (toluene).

Similar to the $\gamma^d$ profiles, the values of $\gamma^b$, determined from the specific interaction free energy of toluene and dichloromethane, are higher for the untreated silica than for the silanized silicas, as displayed in Figure 1c,d. It is calculated that the $\gamma^b$ was reduced between 37 and 91% and between 36 and 52%, for coupling and noncoupling silanes, respectively. From the present study, it is calculated that the total surface energies were reduced between 7 and 50% when the silicas were silanized.

The results indicate that silica surface modification has reduced the number of polar functional groups or has covered the polar energetic sites, and thus could reduce the silica aggregation in the elastomer matrix. S6 (DTSPM) and S8 (TESPO/M) exhibit the lowest $\gamma^b$ and a relatively homogeneous $\gamma^d$ surface profile. This could be due to the coverage of the silica surface by polyether side chains from the DTSPM and by the oligomeric structure of TESPO/M, leading to interaction with the silanol groups on the silica surface through hydrogen bonding, as shown with DTSPM in Figure 2. Both TESPO/M and TESPO have long alkyl groups, which could block the surface, but TESPO/M is likely to be more reactive because of the presence of mercapto groups.34
2.3. Total Work of Cohesion Profiles. The values of the dispersive and specific surface energies of the untreated and modified silica were used to calculate the thermodynamic total work of cohesion \( W_{\text{coh}} \). The \( W_{\text{coh}} \) of the silicas was determined using the determined dispersive \( \gamma_d \) and specific \( \gamma_{sp} \) surface energies. For the present study, the acid \( \gamma_a \) and base \( \gamma_b \) parameters of the polar probes proposed by Della Volpe and Siboni were used. The influence of particle surface energy could be directly related to its role in the reduction of cohesive forces between particles. As shown in Figure 3, \( W_{\text{coh}} \) of S2−S12 was significantly reduced compared to the untreated silica (S1). Thus, the results indicate that the pronounced aggregation of untreated silica will be reduced when the silica is silanized with coupling and noncoupling silanes.

\( W_{\text{coh}} \) between untreated silica particles was determined as 150 mJ/m\(^2\) at 0.1% surface coverage. For similar surface coverage, it was calculated that \( W_{\text{coh}} \) was reduced between 29 and 53% and between 25 and 37%, for silica silanized with coupling and noncoupling silanes, respectively. It is observed again that S6 (DTSPM) and S8 (TESPO/M) showed the largest reduction in \( W_{\text{coh}} \) followed by S7 (TESPO).

The reduction in silica aggregation for treated silica can improve the silica dispersion in the polymer phase, as reported by Ngeow et al. A reduction of 30−40% in silica aggregate size was observed through the transmission electron microscopy (TEM) network visualization technique.

The untreated silica exhibits higher dispersive and specific surface energies compared to the silanized silicas. The values show the higher adsorption energies of untreated silica by a series of \( n \)-alkane molecules. This might indicate a stronger interaction between the nonpolar elastomer and the untreated silica.

In this study, further analysis was carried out to study the effect of total work of cohesion of silica on the silica dispersion efficiency and bound rubber content (BRC) in the elastomer phase. Figure 4 shows that the dispersibility of silica in an
sSBR/BR elastomer matrix was improved with decreasing total work of silica cohesion, achieved by silanization of the silica surface. The measurement of cumulative silica aggregate size distributions in the elastomer vulcanizates was carried out using a network visualization technique.

From Figure 4, the results appear to be split into two groups. In the case of the noncoupling silanes and one of the coupling silanes, TESPO, there is a steady decrease in the aggregate size with decreasing work of silica cohesion, as the silica surface is modified. In the case of the coupling silanes apart from TESPO, all of the modified silicas have similar microdispersions. The aggregate sizes of silica silanized with these coupling silanes were significantly lower than observed with the first group of mainly noncoupling silanes and than expected simply from the decreasing work of cohesion.

A similar split was observed in the correlation between BRC of silica-filled sSBR/BR and total work of silica cohesion, as shown in Figure 5. Lower BRC values were measured for sSBR/BR filled with untreated silica and with silica treated with TESPO (a protected coupling silane) or with noncoupling silanes. This indicates that there may be a second factor improving the microdispersion.

Bound rubber was measured after mixing but before vulcanization. Bonding of the elastomer to the silica, coupling, should occur during vulcanization, but some premature coupling may occur during mixing, which is evidenced by increased BRC. The amount of coupling that occurred during mixing appears to follow the expected order of reactivity of the coupling silanes, i.e., −SH > tetrasulfide > disulfide, with none in the case of the protected TESPO.

Any premature coupling occurring during mixing, however limited, would be expected to increase the viscosity of the compound and thus the shear forces breaking up the silica agglomerates. In addition, the coupling may also lock in the dispersion, preventing reagglomeration, or flocculation, of the filler, which has been reported to occur on storage after mixing. The results suggest that microdispersion is dependent on both the surface properties of the silica and whether any silica–elastomer bonding occurs during the mixing process; its extent will be decided by the end of the mixing process.

3. CONCLUSIONS

In this work, the changes in dispersive and specific silica surface energy when the silica surface is silanized and their effects on microdispersion of the silicas in an sSBR/BR elastomer matrix were investigated. The Φ profiles of untreated silica (S1) show the heterogeneous nature of the silica surface. For this study, running the IGC at finite dilution (FD-IGC) has enabled surface energy mapping of the silica and the total surface energies were reduced between 7 and 50% when the silicas were silanized.

The study has shown that the Wcoh of silica could be used as an indicator of the degree of dispersion of silica aggregates. The study showed that silanizing silica using coupling or non-coupling silanes improves the microdispersion in the elastomer matrix. A small amount of premature coupling during mixing seems to be beneficial, although normally great care is taken to limit premature coupling by controlling the mixing temperature, and indeed silane coupling agents have been developed or proposed specifically to avoid concerns about premature coupling and elastomer cross-linking.

4. EXPERIMENTAL METHODS

4.1. Materials. The silica used for this study was Zeosil 1165 MP (Solvay SA, France) with a Brunauer–Emmett–Teller (BET) specific surface area of 160 m²/g. The silica as supplied contains typically 7% physisorbed water. The elastomers used for this study were oil-extended solution styrene–butadiene rubber (sSBR, VSL 5025-2 HM with 25% styrene and 50% vinyl content, LANXESS Deutschland GmbH, Germany, currently known as ARLANXEO Deutschland GmbH) and cis-1,4-polybutadiene rubber (BR, Europrene Neo cis-BR-40, Versalis, Italy).

As for the silica particle surface modification, bifunctional coupling and monofunctional noncoupling silanes were used for this study. The coupling silanes were bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT, Si 69), 3-(triethoxysilyl)propyl mercaptan (TESPM, VP Si 263), bis[3-(triethoxysilyl)propyl]disulfide (TESPD, VP Si 266), 3-(di-(triethoxycyclopent-ethylenoxy))ethoxyl)propyl mercaptan (DTESPM, VP Si 363), 3-(triethoxysilyl)propyl thio-octanoate (TESPO, NXT), and TESPO/M (a co-oligomer combining, TESPM, TESPO and 1,3-propanediol, NXT Z45). Si 69, Si 263, Si 266, and Si 363 were kindly supplied by Evonik Industries AG, Germany and the NXT silanes by Momentive Performance Materials Inc. The noncoupling silanes were octyltriethoxysilane (OTES, Dynasylan OCTEO), methyltrimethoxysilane (MTMS), methyltriethoxyxilane (MTES), and trimethylethoxilane (TMCS). Dynasylan OCTEO silane was supplied by Evonik Industries AG, Germany and the rest of the noncoupling silanes was purchased from Sigma-Aldrich Co. Ltd., U.K.
The molecular structures of the coupling and noncoupling silanes are shown in Figures 6 and 7. Silanized silica and silica-filled elastomer preparations are described by Ngeow et al.\textsuperscript{41,56}

The grafting of silica particles was performed under a Dean−Stark apparatus experimental setup. The glass reactor was placed in an oil bath and filled with 120 g of silica suspended in 600 mL of toluene. The oil bath was heated to 120 °C for 45 min, and the solution was stirred (with a magnetic stirrer) to reflux the toluene and to remove the physisorbed water from the silica surface. The silane solution (∼15% v/v toluene) was then added.

Figure 6. Molecular structures of bifunctional coupling silanes: (a) TESPT, (b) TESPM, (c) TESPD, (d) DTSPM, (e) TESPO, and (f) TESPO/M used in treated silicas S2−S8.

Figure 7. Molecular structures of noncoupling silanes: (a) OTES, (b) MTMS, (c) MTES, and (d) TMCS used in treated silicas S9−S12.
to the reactor and the mixture was refluxed for 1 h. However, the temperature of the oil bath was lowered to 55 °C for silica silanized with MTMS, MTE, and TMCS, as these silanes have lower boiling points than the toluene. The silanized silica was filtered off, washed with toluene, and dried.

Two loadings of the silane TESPT were used when silanizing the silica, 8% w/w silica (including the physisorbed water), corresponding to the standard amount used in rubber compounding for tire applications, and 12% w/w. The loadings of the other silanes were normalized to the 8% w/w TESPT loading to have the same number of silane groups available for silanization, by taking account of both the molecular weight and the number of silane groups in each molecule. The experiments were carried out three times to study the reproducibility of the silanization.

4.2. Surface Energy Characterization. In IGC, a series of known molecular probes (adsorbates) is injected into a column containing the sample (i.e., powder or fiber) of interest. Helium is used as the carrier gas and methane as a noninteracting or nonadsorbed gas. The elution times of a series of probe molecules provide the surface characteristics of the sample.60–62 Thermodynamic properties of the sample are calculated from the net retention volume, V\text{NO}, such as the standard Gibbs free-energy change of adsorption, ΔG°\text{ad} and the work of adhesion, W\text{adh}.

\[ -\Delta G°\text{ad} = RT \ln V\text{N} + C\text{f} = N\text{A} a\text{m} W\text{adh} \]  

where \( N\text{A} \) is the Avogadro number, \( a\text{m} \) is the molecular cross-sectional area of the adsorbed molecular probe, and \( C\text{f} \) is a constant that depends on the chosen reference state. The \( W\text{adh} \) is related to the surface energy of a material. The total surface free energy, \( \gamma_S \), is a combination of the dispersive component (\( \gamma_{SV} \)) of the surface energy and the specific (acid–base) component (\( \gamma_{SV} \)). For the dispersive component, by applying Fowkes’ relationship, eq 1 leads to

\[ RT \ln V\text{N} = N\text{A} a\text{m} \cdot 2^{1/2} \gamma_{SV}^{1/2} \gamma_{LV}^{1/2} + \text{constant} \]  

\( \gamma_{LV} \) is the dispersive surface energy of the liquid probe. \( \gamma_{SV} \) is the dispersive surface energy of the solid sample and can be calculated from the slope of a linear regression of RT ln \( V\text{N} \) versus \( N\text{A} a\text{m} \gamma_{SV}^{1/2} \gamma_{LV}^{1/2} \), the \( n \)-alkane line, using the approach of Schultz et al.63 The probe molecule orientation and molecular cross-sectional area also may be influenced by temperature effects and may have an impact on the calculated surface energy. Nevertheless, the values obtained here provide for a ranking of the work of cohesion for the silicas as a function of their chemical modification. This trend and the subsequent correlation presented in this work are not skewed due to such effects.

The Gibbs free-energy change of adsorption, \( \Delta G°\text{ad} \), for dispersive and specific (acid–base) components is expressed as the sum of two components

\[ \Delta G°\text{ad} = \Delta G°\text{a} + \Delta G°\text{d} \]  

Therefore, the difference between the alkane regression line and that from the polar molecular probes equates to \( \Delta G°\text{d} \). Using the \( G°\text{d} \) value and by applying the van Oss–Good–Chaudhury (vOCC)64 approach or the Della Volpe theory,15,66 the parameters for acid–base polar interactions can be determined. In this work, the Della Volpe theory of acid–base components is used to determine \( \gamma_{SV}^{d} \). By knowing the surface energies of the individual components, the work of cohesion of silica can be obtained using the following equation

\[ W\text{coh} = 2\gamma_S \]  

where \( \gamma_S \) is the surface energy of the solid. For the present study, the dispersive surface energy of silica is denoted as \( \gamma_{SV}^{d} \) and it is the work of cohesion (eq 4) between solid particles that is of interest.

The filler surface energy determination was carried out using an inverse gas chromatography-surface energy analyzer (IGC-SEA, Surface Measurement Systems Ltd., London, U.K.). For this study, approximately 60 mg of untreated or silanized silica was packed into a standard presilanized column (300 × 2 mm² ID). The untreated or silanized silica was conditioned in situ in the SEA with a helium gas purge at a standard 10 cm³/min (scm) and 0% relative humidity (RH) for 12 h at 110 °C. A series of purely dispersive n-alkane vapor probes, hexane, heptane, octane, nonane, and decane (high-performance liquid chromatography (HPLC) grades, Sigma-Aldrich Co. Ltd., U.K.) was injected into the column held at 90 °C. These probes were injected to cover 0.01–1.0% of the silica particle surface. The details for determination of surface heterogeneity of solid particles are reported in detail elsewhere.

4.3. Silica-Filled Elastomer Compound Preparation. The preparation of the sSBR/BR/silica tire tread compounds, specified in Table 1, was as described previously.56 All except for the TESPT-containing compounds were prepared with 1.5 parts by weight per hundred parts of rubber (pphr) sulfur. TESPT contains labile sulfur that increases the sulfur crosslinking of the elastomer. Consequently, with 8% w/w TESPT the sulfur content was reduced to 1.03 pphr, while with 12% w/w it was reduced to 0.79 pphr.

To mix the sSBR/BR/silica compounds, a three-stage mixing procedure was employed. The mixing was carried out in a Brabender-PolyLab internal mixer fitted with a 350S mixing head with tangential rotors. In the first two stages of mixing
(masterbatch stage and remill stage), the circulating oil temperature was set at 50 °C, the rotor speed was set at 80 revolutions per minute (rpm), and a 0.7 fill factor was used. In the third stage (finalizing stage), the temperature was set at 30 °C with a rotor speed of 50 rpm and the same fill factor (0.7).

In the masterbatch stage (stage 1), the elastomer and 3/4 of the silanized silica were mixed for 2 min, before adding the remaining 1/4 of the silanized silica with process oil and stearic acid and mixing for a further 2 min. The throat of the mixer was then swept and mixing continued for another 2.5 min, followed by dumping after a total mixing time of 6.5 min. In stage 2 (remill stage), zinc oxide and antioxidants were added to the compound from stage 1 at the start and mixing continued for 2 min before dumping. In the finalizing stage (stage 3), the curatives (CBS and sulfur) were added to the compound from stage 2 and mixed for 2 min, followed by dumping.

In this study, all of the compounds used presilanized silica, apart from compound C1, which had no silane. However, normally the silica used in SBR/BR compounds is silanized during mixing. This is referred to as reactive mixing and to ensure sufficient silanization it is recommended to continue the mixing in stage 1 for 4 min or more above 140 °C, with the total mixing time typically 6.5 min.70 For comparison, a similar mixing procedure, with a 6.5 min dump time, was used for all compounds in this study.

4.4. Vulcanized Sheet Preparation. The prepared compounds were vulcanized in a press at 172 °C for 12 min as 9 in. × 9 in. × 2 mm sheets, following BS ISO standards. The vulcanized sheets were used for determination of microdispersion of silica.

4.5. Network Visualization and Silica Microdispersion Analysis. TEM has been used to characterize the distribution of particles within complex arrays, such as filled rubber vulcanizates, by distinguishing between areas occupied by macromolecules and by particles.56,57,70,71 Details of the sample preparation for the network visualization method and the method itself, including evaluation of microdispersion by image analysis of the TEM micrographs, were reported by Chapman et al.56,57,70

Samples of the vulcanizates were extracted in refluxing acetone in a Soxhlet apparatus overnight. The residual solvent was then removed from the samples by drying in a vacuum oven. These samples were then placed in a styrene solution containing 2% w/w di-n-butyl phthalate and 1% w/w benzoyl peroxide for 3 days. After swelling in this solution, the samples were trimmed to about 2 × 2 × 10 mm3 in size and placed in a gelatin capsule filled with a new sample of the same styrene solution. The capsules were placed in a metal heating block and held at 68 °C for a period of 3–5 days, which was sufficient to polymerize the styrene and totally harden the samples.

An RMC PowerTome PC ultramicrotome with a 45° glass knife was used to section the hardened samples at room temperature. Nickel TEM grids were used to collect the sections, which were briefly relaxed with xylene vapor. These sections, approximately 100 nm in thickness, were characterized using a Philips CM12 transmission electron microscope operating at 80 kV.

Analysis of the areas of the silica aggregates in the TEM images of the swollen vulcanizates at 22 000× magnification used the Image Pro Plus 6.1 software. In this study, a total of up to 15 TEM micrographs were analyzed for each vulcanizate, to provide average size distributions of the silica aggregates in the elastomer phases.

The image contrast between the silica and the polymer background was increased by using a background correction and a bandpass filter. Then, a binary variance edge detecting filter was used on the micrograph to locate the edges of the silica aggregates (image 1). A binary image was then generated followed by an open operation to expand the areas encompassing the aggregates (image 2). Merging the two images produced a new image, where the silica aggregates were easier to separate from the background using a segmentation operation. The merged image was used to count and size the silica aggregates.

Macrodispersion analysis evaluates the filler agglomerates normally on a scale between 2 and 100 μm in size, as specified in ASTM D 7723-17. Aggregates observed when evaluating silica microdispersion typically range in size from 15 up to 300 nm. In this study, aggregates larger in area than 100 nm2 were included in the count and aggregates touching the borders were excluded.

4.6. Measurement of the Bound Rubber Content (BRC g/g).56 The uncured compounds were kept for 7 days after the finalizing stage before bound rubber measurements were carried out. A closed glass bottle was used to swell a sample of the uncured compound (approximately 250 mg) in toluene (25 mL) at room temperature over a period of 7 days, with light excluded. The bottle was gently swirled without breaking up the swollen gel during this period. After weighing the swollen gel, it was dried to constant weight at 40 °C. The bound rubber content (BRC) was calculated using eq 5.56

\[
\text{BRC} = \frac{W_{\text{dry gel}} - W_i(m_i/m_f)}{W_i(m_i/m_f)}
\]

where \(W_{\text{dry gel}}\) is the weight of the dry gel, \(W_i\) is the original weight of the sample, \(m_i\) is the relative weight of materials insoluble in toluene in the compound, \(m_f\) is the relative weight of the filler in the compound, and \(m_i\) is the total weight of the compound.

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Notes

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