Novel elastomer dye-functionalised POSS nanocomposites: Enhanced colourimetric, thermomechanical and thermal properties

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Abstract. Nanocomposites consisting of poly(styrene-*b*-butadiene-*b*-styrene) (SBS) and polyhedral oligomeric silsesquioxanes (POSS) were prepared using a solvent dispersion method. POSS molecules were functionalised with two dichlorotriazine reactive dyes (CI Reactive Blue 4, CI Reactive Red 2) prior to compounding. Infrared spectroscopy confirmed functionalisation. Scanning electron microscopy revealed an increase in filler aggregation with concentration, with preferential phase selectivity. Ultraviolet spectroscopy and colourimetry confirmed colour uniformity and suggested that colour intensity could be controlled. Functionalised POSS improved thermal stability by imparting restrictions on SBS chain motions. Tensile stress-strain analysis revealed an increase in modulus with filler concentration, while creep deformation decreased and permanent strain increased with POSS content. Storage modulus, loss modulus and glass transition temperature increased with filler content due to effective SBS-POSS interaction. Nanocomposite properties were influenced by the phase the filler was dispersed throughout and the structure of the dye chromophore.

Keywords: polymer composites, polyhedral oligomeric silsesquioxanes, reactive dye, functionalisation, phase selectivity

1. Introduction

Coloured polymers are utilised in a variety of applications, particularly consumer products, packaging and building materials, due to improved appearance and aesthetic value. The traditional method of producing coloured polymer materials involves directly adding the dye or pigment into the polymer; however this process has several drawbacks. Conventionally coloured polymers can fade, lose colour or experience unexpected colour changes. Dyes may leach from the polymer matrix, lose intensity or bleach due to external factors, such as ultraviolet light, radiation and thermal degradation [1]. To further complicate matters, dispersion of dyes throughout a polymer is difficult, leading to swirling and variation in colour. Poor dispersion can lead to poor mechanical properties. Although compatibilisers

have been used to aid with dispersion, they are expensive and can also be detrimental to mechanical and thermal properties.

One solution is to covalently bond the dye to a stable media and disperse the dye-functionalised particles throughout the polymer. Functionalised-nanoparticles have been prepared by bonding reactive dyes with alumina [1] and silica [2, 3]. Another option is to use polyhedral oligomeric silsesquioxanes (POSS, empirical formula $\text{RSiO}_{1.5}$). These hybrid molecules consist of a rigid inorganic core made up of 8, 10 or 12 silicon atoms linked by oxygen atoms, with organic 'R' substituents attached at the corners of the silica cage. The central core is ceramic in nature, providing thermal stability and rigidity, while the organic groups compatibilise the molecule [4]. First synthesised in 1946 by Scott [5], POSS have begun

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to attract serious attention as a filler material within the last 10 to 15 years, encouraged by the significant improvement in composite properties the fillers provide. Furthermore, a variety of functional groups have been bonded directly onto POSS molecules [6–9]. By preparing dye-functionalised POSS nanoparticles and dispersing them throughout a polymer, the POSS can provide enhanced mechanical and thermal properties and overcome compatibility issues while the dye maintains its functionality, colouring the polymer matrix in the process. The hybrid-pigment will also encouraged dispersion, allowing a degree of control over the functionality and producing a more uniform, stable and visually pleasing material.

Block copolymers have received much academic and industrial attention since the early 1960's, due to low production costs and unique intrinsic properties. In recent times, focus has shifted towards nanotechnology applications, mainly due to the ability of these polymers to form self-assembled domains on the nanometre scale and the ease of which domain size/shape can be manipulated by altering the molecular weight or block concentration [10, 11]. This allows for potential in a number of applications, including biomedical, membrane formation, electronics and information technology [12]. A popular choice of block copolymer is poly(styrene-*b*-butadiene-*b*-styrene) (SBS), a linear triblock-elastomer consisting of hard, glassy polystyrene and soft, rubbery polybutadiene segments. SBS nanocomposites have received much attention in recent years, with fillers including silica, carbon black and montmorillonite clays being incorporated into the

SBS matrix [13–15]. While enhancements in composite properties have been achieved, molecular-level dispersion has been difficult, due to poor matrix-filler compatibility. This can lead to further complications when the objective is to disperse fillers within a particular phase. The incorporation of POSS into SBS has been limited [16–18]. Furthermore, SBS-POSS nanocomposites are usually prepared with grafting reactions. This leaves the opportunity of preparing these nanocomposites using physical blending and to determine whether adequate filler dispersion can be achieved. In addition, the benefit of dispersing the POSS throughout a copolymer, such as SBS, will allow the phase preference of the filler to be observed, due to the compatibilising organic 'R' groups on the POSS molecule.

The aim was to synthesis SBS-POSS nanocomposites via a physical blending process, where the POSS will favour a specific phase of the polymer matrix and enhance composite properties, while the functionality of the dye remains intact. Objectives included functionalising the POSS molecules with dichlorotriazine reactive dyes, preparing SBS-POSS nanocomposites using a solvent dispersion technique and characterising the thermal and mechanical properties of the nanocomposites.

2. Experimental

2.1. Materials

The poly(styrene-*b*-butadiene-*b*-styrene) used as matrix material was Kraton D-1102 (Kraton Polymers LLC). It is a pure, linear triblock copolymer with 29.5 wt% bound styrene and a density of

Table 1. POSS molecule characteristics

POSS	Structure	R group
TrisilanolisobutylPOSS		Isobutyl
TrisilanolphenylPOSS		Phenyl

Table 2. Dye characteristics

Colour index name	Trade name	Structure
CI Reactive Blue 4	Procion Blue MX-R	
CI Reactive Red 2	Procion Red MX-5B	

0.938 g·cm³. Two types of POSS were used as fillers; Trisilanophenyl POSS and Trisilanolisobutyl POSS. Both were supplied by Hybrid Plastics Inc. and their specifications are listed in Table 1. Two varieties of dichlorotriazine dye were reacted with the POSS molecules, CI Reactive Blue 4 (Procion Blue MX-R) and CI Reactive Red 2 (Procion Red MX-B5), obtained from Kraft Colour Pty Ltd., Whittlesea, Australia. The structures and details of the dyes are shown in Table 2. 3-aminopropyltriethoxysilane and diisopropylethylamine were obtained from

Aldrich Chemical Co., Milwaukee, USA. All chemicals were used as received.

2.2. Preparation of dye-functionalised POSS

2.2.1. Preparation of 3-amino treated POSS

Figure 1 shows the preparation of dye-functionalised POSS. 3-Aminopropyltriethoxysilane (10 mL) was dissolved in 100 mL of toluene. Trisilanol POSS was added while the solution was vigorously stirred. The reaction suspension was subjected to ultrasonic disruption (20 kHz, 10 min, 25°C) then refluxed for

Figure 1. Preparation of dye-functionalised POSS

3 h. After being left at ambient overnight to allow the toluene to evaporate, the recovered POSS was washed with toluene, followed by methanol and acetone, respectively. The POSS was dried in a vacuum oven at 80°C for 12 h and kept in a desiccator over silica gel.

2.2.2. Reaction of dichlorotriazine dyes with treated POSS

To 50 mL of dichloromethane, the amino-functionalised POSS (5 g), dichlorotriazine dye (5 wt%) and diisopropylethylamine (5 mL) were added. The solution was stirred at 35°C for 1 h. The POSS-dye hybrid was filtered, washed with methanol and stored in a desiccator over silica gel.

2.3. Preparation of SBS-POSS nanocomposites

Nanocomposites with various functionalised-POSS concentrations (1, 5, 10, 20 wt%) were prepared using a solvent dispersion technique. SBS was dissolved in 150 mL of dichloromethane and vigorously stirred for 1 h at 25°C, until the polymer was completely dissolved. POSS was added to the solution and subjected to ultrasonic disruption (20 kHz, 10 min, 25°C) to ensure even distribution of the filler throughout the matrix. The solution was poured into an excess of cold methanol to precipitate the nanocomposite material and to restrict filler migration. The composite was isolated using suction filtration and dried in a desiccator overnight. Films for subsequent use were prepared using a heated press (IDM Instruments Inc., model number L0003-1). Films were heated to 150°C, 6 tonnes of pressure applied, held for 2 min and cooled to ambient.

The nomenclature for the nanocomposites is SBS-*x*POSS-*y* *z*, where *x* corresponds to the functional groups on the POSS (phenyl or isobutyl), *y* is the dye that POSS was reacted with (blue or red) and *z* equals the amount of POSS or functionalised POSS within the composite by wt%.

2.4. Characterisation of nanocomposites

2.4.1. Structural analysis

A Perkin-Elmer Spectrum 2000 FTIR spectrometer working in diffuse reflectance spectroscopy (DRIFTS) mode was used to characterise the molecular vibration of the functional groups in the POSS

and reactive dyes. Anhydrous potassium bromide (KBr) was used as dispersing material and all spectra were scanned within the range 400–4000 cm⁻¹, with a total of 20 scans and a resolution of 8 cm⁻¹.

2.4.2. Morphological analysis

Scanning electron microscopy (SEM) images of the nanocomposites were taken using a FEI Quanta 200 environmental scanning electron microscope (ESEM) operating at 20 kV. Composites with average dimensions ~4.00×4.00×0.70 mm³ were mounted to the specimen holder using carbon tape.

2.4.3. Thermal analysis

A Perkin-Elmer TGA-7 thermogravimetric analyser was used to analyse the thermal stability of the nanocomposites. Samples of ~10 mg were heated to 850°C at 20°C·min⁻¹ in an inert environment provided by a 20 mL·min⁻¹ nitrogen purge. The mass loss and its derivative were recorded as a function of temperature.

2.4.4. Visible spectroscopy

A Varian 50 Bio UV-visible spectrophotometer was used to analyse the absorbance properties of the nanocomposites. Composites were scanned over a wavelength range of 800 to 200 nm using a dual beam at a scan rate of 108 nm·min⁻¹. The composites had an average thickness of ~0.70 mm and the results presented are the average of five replicates.

2.4.5. Colourimetry

A Konica Minolta CR-400 Chroma Meter was used to analyse the colourimetric properties of the dye-functionalised nanocomposites. CIELAB (*L*^{*}, *a*^{*}, *b*^{*}) colour space coordinates were obtained, with results presented being the average of 10 measurements. A white ceramic tile (*Y* = 93.9, *x* = 0.3134, *y* = 0.3197) was used as a calibration reference.

2.4.6. Thermomechanical analysis

Thermomechanical analysis was performed using a TA Instruments Q800 Dynamic Mechanical Analyser in tensile mode to analyse the elastic properties of the composite films. Rectangular films of ~12.80 × 4.00 × 0.70 mm³ were subjected to stress-strain, creep-recovery and modulated force-thermo-mechanometry.

Stress-strain

Stress-strain (dynamic force-thermomechanometry, df-TM) analysis was performed using an initial force of 10 mN followed by an applied force increasing at a rate of $1 \text{ N} \cdot \text{min}^{-1}$, reaching a maximum of 18 N. Tests were conducted under ambient conditions (30°C) to determine the linear viscoelastic region and elastic modulus. Results presented are the average of triplicate measurements.

Creep-recovery

Creep-recovery (static force-thermomechanometry, sf-TM) analysis was performed by subjecting films to an applied stress of 0.5 MPa for 20 min, followed by a recovery period of 80 min with 0.01 MPa applied stress. The applied stress chosen was within the linear viscoelastic region of all the nanocomposites. Tests were conducted at ambient temperature (30°C) and all results presented are the average of triplicate measurements. The four-element model of Maxwell and Kelvin-Voigt (Figure 2) was used to interpret the creep component. The springs correspond to elastic sections with moduli E_1 and E_2 , while the dashpots represent the viscosity (η_1 , η_2). The overall deformation of the model is given in Equation (1):

$$\varepsilon(f) = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{\eta_1} + \frac{\sigma_0}{E_2} (1 - e^{-t/(\eta_2/E_2)}) \quad (1)$$

The stretched exponential function of Kohlrausch, Williams and Watts [19] (KWW) was used to interpret the recovery behaviour and is given in Equation (2):

$$\phi = A \exp^{-(t/\tau)^\beta} \quad (2)$$

Figure 2. The four-element model

where A is the pre-exponential coefficient, t is time, τ is the retardation time and β is the non-linearity coefficient ($0 < \beta < 1$).

Elastic and viscoelastic properties

Modulated force-thermomechanometry (mf-TM) analysis was conducted using a static force of 500 mN, modulated force of 100 mN and frequency of 1 Hz. The storage modulus (E'), loss modulus (E''), loss tangent ($\tan \delta$) and associated glass transition (T_g) temperatures of the films were measured as a function of temperature from -100 to 110°C at a heating rate of $2^\circ\text{C} \cdot \text{min}^{-1}$.

3. Results and discussion

3.1. Chemical structure of dye-functionalised POSS

FTIR spectroscopy was used to confirm the chemical structure formed by the reaction of POSS and the reactive dyes, to determine whether bonding between the respective molecules was achieved. The infrared spectra of the untreated POSS and dyes are shown in Figure 3a. The pure POSS shows several bands characteristic of their structure; 3154 cm^{-1} (hydroxyl (OH) stretching vibrations), 1100 and 890 cm^{-1} (Si–O–Si and SiOH stretching vibrations). TrisilanophenylPOSS displays bands at 1594 , 1490 and 1430 cm^{-1} , corresponding to vibrational stretching of the C=C bonds within the phenyl ‘R’ groups. The three bands in this region confirm the presence of a conjugated phenyl system. Other bands corresponding to the trisilanophenylPOSS structure include 3070 cm^{-1} (sp^2 CH stretching vibrations), 696 and 740 cm^{-1} (C–H bending vibrations). TrisilanolisobutylPOSS exhibits strong bands at 2950 , 2900 and 2868 cm^{-1} , corresponding to vibrational stretching of the CH_3 , CH_2 and CH groups of the isobutyl ‘R’ groups. Other peaks specific to isobutyl include those at 1462 , 1400 , 1366 and 1328 cm^{-1} , correlating to CH_2 and CH_3 bending vibrations and deformation.

The reactive dyes exhibited several bands indicative of the functionality/segments common in both structures; 3436 cm^{-1} (N–H stretching vibrations), 3064 cm^{-1} (C–N symmetric stretching), 2924 cm^{-1} (C–N asymmetric stretching), 1212 cm^{-1} (C–N stretching vibrations), 1042 cm^{-1} (S=O stretching vibrations) and 678 cm^{-1} (C–Cl stretching). CI Reactive Blue 4 displays additional bands specific

Figure 3. (a) Infrared spectrographs of raw materials; (i) TrisilanolphenylPOSS, (ii) TrisilanolisobutylPOSS, (iii) CI Reactive Red 2, (iv) CI Reactive Blue 4, (b) infrared spectrographs of functionalised POSS; (i) ibPOSS-blue, (ii) ibPOSS-red, (iii) phPOSS-blue, (iv) phPOSS-red

to its structure at 3258 cm^{-1} (N–H stretching vibrations for secondary amines), 1538 cm^{-1} (NH_2 scissoring), 1718 cm^{-1} (C=O stretching for saturated ketones) and 1404 cm^{-1} (SO_3H stretching vibrations). CI Reactive Red 2 displayed additional characteristic peaks at 1534 cm^{-1} (N=N stretching of the azo group), 862 and 964 cm^{-1} (NH_2 and NH wagging – shifts on H-bonding).

The infrared spectrographs of the dye-functionalised POSS nanoparticles are shown in Figure 3b. For all nanoparticles, a noticeable reduction in peak size is noticed at 3154 cm^{-1} . This indicates a reduction in the number of OH groups on the POSS molecules, suggesting that bonding has occurred with the reactive dyes. Strong peaks are observed at 1100 cm^{-1} , confirming the presence of Si–O bonds. Both isobutylPOSS pigments display bands at 2950 and 2868 cm^{-1} , confirming the presence of isobutyl groups. Similarly, phenylPOSS pigments displayed characteristic peaks at 3044 cm^{-1} (CH stretching vibrations) and 1580 , 1554 and 1542 cm^{-1} (C=C vibrational stretching of phenyl groups). The presence of the reacted dyes was confirmed by the occurrence of several characteristic peaks in all functionalised POSS; 3296 cm^{-1} (NH stretching vibrations), 1558 cm^{-1} (NH_2 scissoring), 1546 cm^{-1} (NH bending vibrations) and 700 cm^{-1} (C–Cl stretching). These observations confirm that covalent bonding has occurred between the amino-treated trisilanolPOSS and reactive dyes.

3.2. Morphology

Scanning electron microscopy (SEM) was employed to investigate the morphology of the nanocompos-

ites. The micrographs are presented in Figure 4. Incorporation of up to 5 wt% POSS into the SBS resulted in a relatively uniform distribution of filler throughout the matrix, with POSS clustering into small agglomerates with an average diameter of $\sim 0.08\text{--}0.1\text{ }\mu\text{m}$. As the concentration of POSS increased, so too did the occurrence of agglomeration, ranging from few small instances at 5 wt% (Figure 4a) to the formation of large agglomerates at 20 wt% with average diameters of $\sim 0.6\text{--}0.7\text{ }\mu\text{m}$ (Figure 4b). Despite utilising ultrasonic disruption to discourage filler clustering and polymer precipitation to ‘trap’ the filler in place, the micrographs indicate that at POSS concentrations greater than 5 wt%, interactions between the functionalised POSS nanoparticles are quite strong and can withstand physical methods used to encourage particle separation. These interactions are usually in the form of Coulomb and van der Waals forces.

Figure 4c and 4d display the micrographs of SBS-ibPOSS-red 5 and SBS-phPOSS-red 5, respectively. Incorporation of 5 wt% red-functionalised isobutylPOSS gives an even distribution of filler throughout the matrix, with small clusters of $\sim 0.1\text{--}0.2\text{ }\mu\text{m}$. Conversely, addition of phenylPOSS at the same concentration and functionalised with the same dye leads to an increase in the development of agglomeration, with larger clusters of $\sim 0.4\text{--}0.6\text{ }\mu\text{m}$ occurring. This behaviour is attributed to the corner ‘R’ groups on the silsesquioxane cages, which determine phase compatibility and, therefore, morphology. As noted previously, the bulk of the SBS matrix used consists of polybutadiene ($\sim 70.5\text{ wt}\%$), providing POSS cages with isobutyl ‘R’ groups a

Figure 4. Scanning electron micrographs of SBS-POSS nanocomposites; (a) ibPOSS-blue 5, (b) ibPOSS-blue 20, (c) ibPOSS-red 5 (d) phPOSS-red 5

relatively large volume to disperse throughout and occupy. This was in contrast to phenylPOSS, which by comparison has a significantly smaller volume of polymer (styrene phase) to occupy, leading to increased interactions between the POSS molecules due to their proximity. This leads to the formation of larger agglomerates within the fewer styrene domains available and correlates to observations in SBS-dumbbell POSS composites. This provides complimentary details reinforcing the phase preference behaviour is still being maintained, even with the addition of dichlorotriazine reactive dyes.

3.3. Optical properties of SBS dye-functionalised POSS composites

3.3.1. Colourimetry

The CIELAB (L^* , a^* , b^*) colour space coordinates of SBS and the dye-functionalised nanocomposites are presented in Table 3. The L^* coordinate represents the whiteness of the material (0 = black, 100 = white). Pure SBS displayed an L^* value of 94.13, indicative of its transparency. The nanocomposites became more translucent and intense in colour with increasing functionalised-POSS content, which was characterised by a decrease in the value of L^* . This

Table 3. CIELAB colour space co-ordinates of SBS-POSS nanocomposites

Material	L^*	a^*	b^*
SBS	94.13	0.00	2.74
ibPOSS-blue 1	82.49	0.36	−10.78
ibPOSS-blue 5	44.43	6.49	−32.94
ibPOSS-blue 10	34.94	9.50	−36.42
ibPOSS-blue 20	23.87	14.23	−37.78
ibPOSS-red 1	80.38	25.21	−4.73
ibPOSS-red 5	53.09	59.17	1.70
ibPOSS-red 10	42.38	61.11	14.93
ibPOSS-red 20	30.22	62.80	16.37
phPOSS-blue 1	87.63	0.06	−4.02
phPOSS-blue 5	68.67	1.54	−24.56
phPOSS-blue 10	46.48	6.76	−31.22
phPOSS-blue 20	28.37	12.85	−35.87
phPOSS-red 1	88.67	9.14	−3.67
phPOSS-red 5	70.68	35.25	0.52
phPOSS-red 10	53.72	54.89	1.48
phPOSS-red 20	39.62	58.86	10.98

was expected since a higher filler concentration causes an increase in the number of bound-dye molecules dispersed throughout the polymer. Isobutyl-POSS nanocomposites yielded lower L^* than their phenylPOSS counterparts at the same concentration, attributed to the dispersion of POSS (and dye) throughout the continuous, polybutadiene phase. The a^* coordinate provides an indication of the colour's position between red and green (negative = green, positive = red) while the b^* coordinate gives the position between blue and yellow (negative = blue, positive = yellow). Nanocomposites containing POSS functionalised with CI Reactive Blue 4 displayed a^* values which gradually became more positive with filler content and b^* values which rapidly became negative. This correlated well with the increasing intensity of blue colour which developed throughout the polymer with the increase in functionalised-POSS concentration. Materials containing CI Reactive Red 2 functionalised-POSS yielded a^* and b^* values which both became positive. As with their blue dye counterparts, this behaviour was accompanied by an increase in colour intensity with filler content. In particular, b^* values leveled-off at higher filler loadings, due to limited dispersion throughout the SBS matrix.

Composites with filler loadings of 1 and 5 wt% visually displayed a uniform and even distribution of colour. As the concentration increased to 10 and 20 wt%, the quality of colourimetric properties began to decline, with pigment specks and minor

swirling being observed. This deterioration in visual appearance was more evident in phenylPOSS composites than those containing isobutylPOSS and can be attributed to the degree of filler dispersion. Furthermore, interactions between auxochromes (NH_2 , SO_3H and $\text{C}=\text{O}$ on CI Reactive Blue 4, SO_3Na and OH on CI Reactive Red 2) may result in filler agglomeration. Colour-producing ability is proportional to the amount of pigment surface that can interact with light. Thus, the ability of a pigment to selectively absorb specific wavelengths of light increases with decreasing particle size, reaching optimal values when the particle is completely penetrated by light [20]. Due to the structural composition of SBS, POSS containing isobutyl 'R' compatibilising groups have greater phase volume to disperse throughout compared with phenylPOSS. This greater degree of volume reduces the probability of agglomerate formation, particularly at higher filler loadings (10 and 20 wt%). The 'dye-functionalised POSS chromophores' are not transparent (the pure POSS particles are white) and lack optimal light-absorption properties, due to their tendency to cluster at higher filler loadings. The chromophores were not surface-treated for two reasons; (1) to leave the visual properties of the dye unchanged and (2) to not compromise the mechanical or thermal properties of the composite. The colourimetric results indicate that although the colour intensity can be increased, consistency and uniformity decrease at dye-functionalised POSS concentrations past 5 wt%.

3.3.2. UV-visible spectroscopy

The UV absorbance spectra of various SBS-POSS nanocomposites are shown in Figure 5. Nanocomposites containing CI Reactive Red 2-functionalised POSS (Figure 5a) displayed absorption spectra indicative of a red dye/pigment, with strong peaks at ~520 and 550 nm (green absorption) and a weaker band at ~370 nm (violet absorption). Little-to-no absorbance was observed across the red wavelength region (620–750 nm), indicative of the reflectance of red light by the chromophore. Absorbance intensity increased with filler concentration, due to the increased number of dye-functionalised POSS segments able to absorb and reflect light. The incorporation of CI Reactive Blue 4-functionalised POSS into SBS yielded strong peaks at

Figure 5. (a) Absorbance spectra of ibPOSS-red composites, (b) absorbance spectra of ibPOSS-blue composites, (c) absorbance spectra of 5 wt% filled composites

~600 and 630 nm (absorption of orange/red), with an additional weaker wavelength band at ~375 nm (violet absorption), as shown in Figure 5b. A large trough was observed at ~450 nm, indicating the reflectance of blue light. The intensity of the UV absorbance increased with filler concentration, which correlated with the increase in colour intensity observed at higher filler concentrations.

A significant difference in the absorbance properties of both blue- and red-dye functionalised materials was clearly observed in the nanocomposites derived from isobutylPOSS and phenylPOSS. Composites prepared with isobutylPOSS exhibited greater absorbance peaks compared with phenylPOSS, this behaviour attributed to the compatibility and dispersion of the respective functionalised fillers within SBS. Although ultrasonic disruption was used in an attempt to obtain a full dispersion of particles throughout the matrix, specific interactions between particles and phase preference limited the ability to obtain the optimal level of dispersion desired. Ideally, when adding dyes or pigments into a polymer, the goal is to achieve full dispersion of particles throughout the matrix, since this gives the highest possible colour strength [21].

IsobutylPOSS was observed to exhibit a stronger affinity to disperse throughout the butadiene phase, due to compatibility of the POSS ‘R’ groups, greater phase volume for dispersion and reduced probability of agglomerate formation. Similar behaviour of phase selectivity manifested, resulting in the UV-visible characteristics shown in Figure 5c. Materials containing dye-functionalised isobutylPOSS (both red and blue) exhibited greater absorbance intensity because of the smaller particle domains being dispersed within the main phase of SBS, allowing for a greater amount of light absorption. This yielded films with a fuller, more intense colour. In contrast, dye-functionalised phenylPOSS, with a preference for the styrene phase, have a more constrained local environment local environment to disperse the particles and may increase the likelihood of aggregate formation, leading to inferior light-absorption properties. Interactions between chromophores may also lead to filler clustering. The UV-visible spectroscopy results correlate to the increase in colour intensity observed using colourimetry and reiterate that filler dispersion is the primary factor which dictates visual properties.

3.4. Thermal stability

The mass loss versus temperature curves of pure SBS and nanocomposites are shown in Figure 6. The decomposition of SBS shows one degradation step at ~454°C. The thermal degradation mechanism of SBS consists of two main processes, namely chain scission and crosslinking [22]. As listed in

Figure 6. Mass loss curves of SBS-dye functionalised POSS composites; (a) ibPOSS-blue composites, (b) 10 wt% filled composites

Table 4. T_d values of SBS and SBS-POSS nanocomposites

Material	T_d [°C]
SBS	454
ibPOSS-blue 1	454
ibPOSS-blue 5	458
ibPOSS-blue 10	461
ibPOSS-blue 20	462
ibPOSS-red 1	455
ibPOSS-red 5	456
ibPOSS-red 10	458
ibPOSS-red 20	460
phPOSS-blue 1	456
phPOSS-blue 5	457
phPOSS-blue 10	457
phPOSS-blue 20	460
phPOSS-red 1	455
phPOSS-red 5	455
phPOSS-red 10	457
phPOSS-red 20	458

Table 4, incorporation of functionalised POSS into the SBS matrix increased the temperature at which the maximum rate of degradation occurs (T_d), with nanocomposites containing 1 wt% isobutylPOSS yielding T_d values ranging from 455–456°C. T_d continued to increase with filler content, reaching a maximum of 463°C in SBS-ibPOSS-blue-20. This behaviour is characteristic of the thermal stability of POSS which stems from its silicon-oxygen structure. A proposed mechanism of thermal reinforcement is that POSS molecules restrict polymer chain motions, due to polymer-filler interactions or by the large inertia exhibited by segments of polymer containing POSS [23, 24]. The compatibilising ‘R’ groups on the POSS encourage this interfacial interaction, allowing thermal reinforcement to be achieved. This is especially important given the

organic nature of the reactive dyes, which undergo thermal degradation at temperatures well below that of SBS. The improved thermal stability despite the presence of ‘volatile’ reactive dyes suggests effective matrix-POSS interactions and adequate thermal reinforcement by POSS molecules.

Negligible differences were observed between nanocomposites containing isobutylPOSS and phenylPOSS at concentrations of 1–5 wt%. At filler concentrations of 10 and 20 wt%, isobutylPOSS nanocomposites exhibited slightly higher T_d values than their phenylPOSS counterparts, as shown in Figure 6b. The behaviour is attributed to the dispersion of POSS within a particular phase of the SBS matrix. The thermal stability of SBS is dependent on the sensitivity of the double bonds within the continuous, butadiene phase [22, 25]. When dispersed throughout the rubber phase, POSS imparts added stiffness into the matrix by acting as crosslink points and reducing chain mobility [26, 27]. This provides thermal stability to the phase upon which the thermal degradation mechanism is dependent. Similarly, little difference was observed between materials containing blue and red dye-functionalised POSS at concentrations of 1–5 wt%. However, at higher filler loadings (10 and 20 wt%), nanocomposites containing POSS functionalised with CI Reactive Blue 4 displayed T_d values ~2–3°C higher than their CI Reactive Red 2 counterparts. Although TGA precision may account for the difference in thermal stability at higher filler concentrations, chromophore structures of the reactive dyes may also be a factor. The chromophore of CI Reactive Blue 4 is based on anthracene which is known to be quite thermally stable [28, 29]. In con-

trast, CI Reactive Red 2 contains a less-stable, naphthalene-based chromophore, which experiences thermal degradation at lower temperatures. These results indicate that thermal degradation behaviour is dependent on both the phase in which the POSS is dispersed and the structure of the bonded reactive dyes.

3.5. Thermomechanical analysis

3.5.1. Stress-strain analysis

The elastic moduli (E) of SBS and nanocomposites are presented in Figure 7. The matrix of SBS exhibited an E of 189 Pa. Addition of POSS had a positive effect on E , which increased with filler concentration, reaching a maximum at 5 wt% POSS content. The increase is characteristic of the reinforcement ability of POSS. The applied stress was transferred from the SBS matrix to the POSS filler resulting in increased strength and stiffness. This stress-transfer process was aided by sufficient interfacial adhesion between the matrix and filler, achieved through compatibilising 'R' groups on the POSS molecules. Furthermore, the dispersion obtained for these low filler nanocomposites throughout the SBS matrix contributed to the improved mechanical properties. Higher POSS concentrations (10 and 20 wt%) caused a decrease in E values. There are several possible reasons for the mechanical E reduction in higher filled nanocomposites. Verker *et al* [30] and Zhao and Schiraldi [31] attributed similar behaviour to a disruption of the polymer molecular (chain) structure brought on by POSS concentrations above 5 wt%. Liu and Zheng [32] suggested this observation is caused by a decrease in material density, due to an increase in nanocomposite porosity [33, 34]. Additionally, the crosslinking densities per unit vol-

ume can decrease with increasing POSS content, compromising the reinforcement mechanism as a consequence. The observed reduction in modulus is most probably caused by such reasons, that may be induced by filler agglomeration affecting the SBS-filler mechanisms that would normally provide good reinforcement. The agglomeration of pigment-pigment clusters, along with reduced effective crosslinking densities and potential voids deteriorate the mechanical properties, resulting in decreased modulus values [35, 36]. Furthermore, agglomerated pigment clusters can act as stress concentrators, causing premature mechanical failure. This correlates to the deterioration in optical properties associated with clustering at filler loadings above 5 wt%.

IsobutylPOSS composites yielded the greatest modulus values. This was attributed to the dispersion of POSS within the polybutadiene (rubber) phase of the SBS, facilitated by the isobutyl 'R' groups on the POSS molecule. The styrene domains within SBS act as cross-links, restricting the flow of the rubber phase and providing strength and durability. Incorporating POSS into the rubber phase provides additional reinforcement, allowing for greater amounts of stress to be transferred from the polybutadiene. The E increased with filler content, ranging from 278 and 283 Pa for 1 wt% composites of isobutyl-POSS-blue and isobutylPOSS-red, respectively, to 570 and 549 Pa for their respective 5 wt% counterparts. PhenylPOSS composites exhibited lower modulus values than composites containing isobutyl-POSS, due to the phenyl 'R' groups on the POSS molecules which provide an affinity towards the glassy, polystyrene segments within the SBS. This reduces the chance of POSS being dispersed throughout the continuous polybutadiene phase and providing adequate reinforcement. No clear distinction between the effects of the two dyes was observed.

Figure 8 shows the tensile strength at yield of the nanocomposites. Similar trends were observed as per the elastic modulus, with the tensile strength at yield reaching a maximum value at 5 wt% for all nanocomposites. POSS concentrations up to and including 5 wt% provide enhanced toughness and strength by allowing sufficient stress transfer to occur. At higher concentrations, aggregation amongst the POSS particles occurred. This resulted in the possible formation of voids within the SBS-POSS

Figure 7. Elastic modulus of SBS and SBS-POSS nanocomposites

Figure 8. Tensile strength at yield of SBS and SBS-POSS nanocomposites

Figure 9. Elongation at yield of SBS and SBS-POSS nanocomposites

interface and the reduction in tensile strength [37]. Composites containing isobutylPOSS exhibited slightly higher values than their phenylPOSS equivalents, due to the increased reinforcement ability when POSS was dispersed throughout the continuous phase of the SBS. As a consequence of the higher modulus, elongation at yield (Figure 9) decreased with increasing POSS content for all nanocomposites. The incorporation of rigid nanoparticles into an

elastomer imparts stiffness, decreasing the elasticity and ductility.

3.5.2. Creep-recovery analysis

The creep-recovery curves of SBS and ibPOSS-red filled composites are shown in Figure 10a. Creep deformation decreased with increasing POSS content. This was expected of an elastomer filled with rigid reinforcement. Due to its ceramic silica structure, the presence of POSS imparts stiffness into the matrix. This restricts the molecular motions of the polybutadiene chains, resulting in less deformation. Furthermore, the compatibilising organic groups on the POSS encourage further interaction and adhesion between the matrix and filler, allowing for the nanocomposites to withstand greater levels of stress without experiencing deformation. At higher POSS loadings (10 and 20 wt%), nanocomposites exhibited flatter creep curves with a lower viscosity component, indicating a decrease of deformation of the elastic component. Nanocomposites containing isobutylPOSS exhibited less deformation than their phenylPOSS counterparts, which was in agreement with the stress-strain results. Since the polybutadiene chains which comprise the rubbery, continuous phase experience molecular rearrangement and motions under stress, it is more effective to disperse filler throughout this phase in order to reduce deformation.

When comparing the curves of the blue and red dye-nanocomposites (Figure 10b), a significant difference in creep behaviour is evident. Nanocomposites containing POSS functionalised with CI Reactive Blue 4 showed considerably less creep and deformation than those containing CI Reactive Red 2. This occurrence can be attributed to the dif-

Figure 10. (a) Creep-recovery curves of ibPOSS-red nanocomposites, (b) creep-recovery curves of 10 wt% filled nanocomposites

ference in chromophore structure of the dyes (refer Table 2). The anthracene-based chromophore of CI Reactive Blue 4 is considerably bulkier and extends further from the dichlorotriazine reactive group than the naphthalene-based chromophore of CI Reactive Red 2. These features provide additional restraints on molecular motions, resulting in the matrix exhibiting less creep and deformation. Hence the dye can impart some physical constraints to dimensional stability.

The parameters of the four-element model were calculated for the creep component of SBS and the nanocomposites, which is presented in Table 5. The Maxwell modulus (E_1) was observed to increase with POSS content, confirming that the nano-sized fillers influence the flow of the SBS matrix. This behaviour correlates to an increase in Maxwell viscosity (η_1), which indicates improved resistance to deformation. Nanocomposites containing isobutyl-POSS displayed larger E_1 and η_1 values than their phenylPOSS counterparts treated with the same dye. Similarly, composites with CI Reactive Blue 4-functionalised POSS yielded higher values than those functionalised with CI Reactive Red 2. These parameters provide an accurate representation of what was observed experimentally. All materials displayed a certain proportion of unrecovered strain that is characteristic of viscoelastic materials such as SBS. This is due to irreversible chain entanglement slippage and detachment of styrene domains from the polybutadiene rubber-phase which occurs

during the application of load. Permanent deformation increased with POSS concentration, with nanocomposites containing blue-functionalised isobutyl-POSS displaying the largest values. Higher concentrations of filler, such as POSS, restrict the relaxation of SBS chains, causing irreversible chain slippage and unravelling. The Voigt viscosity (η_2) was observed to increase with POSS content, suggesting an increase in resistance of the SBS chains to uncoiling.

Increasing the POSS content caused the τ to decrease, suggesting that the nanocomposites become more solid-like in behaviour at higher filler concentrations. Similarly, highly filled composites exhibited flatter recovery curves, indicating a faster recovery of the viscoelastic component. Nanocomposites containing phenylPOSS displayed slightly longer τ than their isobutylPOSS counterparts treated with the same-coloured dye. When rubbery, polybutadiene chains are highly stretched under an applied load, phenylPOSS molecules can become detached from the glassy styrene domains for which they have an affinity. This can lead to dissimilar block-mixing occurring in interfacial regions, causing an increase in permanent deformation [38]. Nanocomposites functionalised with CI Reactive Blue 4 yielded longer τ than those functionalised with CI Reactive Red 2. This was once again attributed to the increased restrictions placed on segmental motions for relaxation by the bulkier, blue-coloured chromophore, causing the material to behave in a more solid-like nature. These results correlate well to the

Table 5. Creep-recovery data of SBS and SBS-POSS nanocomposites

Material	E_1 [MPa]	η_1 [MPa·s ⁻¹]	E_2 [MPa]	η_2 [MPa·s ⁻¹]	τ [min]	Permanent deformation [%]
SBS	0.22	67.91	0.35	3.31	9.46	18
ibPOSS-blue 1	0.26	77.04	0.74	6.17	8.33	23
ibPOSS-blue 5	0.34	85.06	1.24	8.79	7.09	29
ibPOSS-blue 10	0.57	103.79	1.58	13.65	6.94	33
ibPOSS-blue 20	0.81	154.36	2.48	16.37	6.60	37
ibPOSS-red 1	0.22	72.77	0.65	5.70	8.77	23
ibPOSS-red 5	0.26	78.84	0.87	7.03	8.08	25
ibPOSS-red 10	0.47	91.32	1.08	8.53	7.90	30
ibPOSS-red 20	0.47	138.25	1.62	11.43	7.05	34
phPOSS-blue 1	0.20	73.61	0.71	6.09	8.58	20
phPOSS-blue 5	0.31	80.81	1.14	8.53	7.48	28
phPOSS-blue 10	0.43	104.67	1.47	10.66	7.25	32
phPOSS-blue 20	0.71	145.64	2.16	14.95	6.92	34
phPOSS-red 1	0.21	70.92	0.48	4.35	9.06	19
phPOSS-red 5	0.22	72.24	0.73	6.58	9.01	21
phPOSS-red 10	0.35	89.31	0.99	8.37	8.45	24
phPOSS-red 20	0.44	133.70	1.33	10.97	8.24	29

Table 6. KWW parameters of SBS and SBS-POSS nanocomposites

Material	A	β	τ [s]
SBS	3.18	0.14	35.74
ibPOSS-blue 1	2.36	0.09	30.84
ibPOSS-blue 5	1.91	0.04	24.97
ibPOSS-blue 10	1.05	0.01	15.60
ibPOSS-blue 20	0.84	0.01	12.20
ibPOSS-red 1	2.66	0.10	27.60
ibPOSS-red 5	2.39	0.07	24.60
ibPOSS-red 10	2.48	0.05	23.40
ibPOSS-red 20	2.10	0.04	18.10
phPOSS-blue 1	2.54	0.11	32.90
phPOSS-blue 5	2.16	0.05	24.70
phPOSS-blue 10	1.56	0.03	20.40
phPOSS-blue 20	1.34	0.02	17.60
phPOSS-red 1	2.94	0.12	31.50
phPOSS-red 5	2.31	0.09	27.90
phPOSS-red 10	1.77	0.06	23.00
phPOSS-red 20	1.29	0.04	17.80

behaviour observed in the creep component and stress-strain analysis, with the time scale allowing the more subtle effects of phase preference, filler concentration and chromophore structure to become observable.

In order to further examine relaxation behaviour, the KWW stretched exponential function was applied to SBS and the nanocomposites. The results are presented in Table 6. In fitting the function, the pre-exponential constant and relaxation time decreased with increasing POSS content. This was to be expected since the relaxation provides an indication of the degree of mobility molecules within the polymer possess. The decreased relaxation time at higher POSS concentrations is indicative of the solid-like behaviour highly-filled nanocomposites exhibit and is in agreement with the creep data obtained using the four-element model. Correspondingly, the shape fitting parameter β changed with POSS content. The value of β is influenced by various factors, including structure, the presence of fillers, crosslinks and crystallinity [39]. These observations strongly suggest that the nanocomposites experience restricted flow, attributed to the incorporation of functionalised-POSS.

3.5.3. Modulated force-thermomechanometry

Figure 11 shows the storage modulus (E') of SBS and selected nanocomposites. Nanocomposites containing POSS displayed higher E' values than pure

Figure 11. Storage modulus (E') curves across the polybutadiene glass-rubber transition of SBS and ibPOSS-filled composites. Inset shows the E' behaviour above the polybutadiene T_g

SBS. The E' modulus reached a maximum at POSS concentrations of 5 wt%, with SBS-ibPOSS-blue 5 and SBS-ibPOSS-red 5 exhibiting E' values of 3.1 and 2.8 GPa at -90°C , respectively. Similar observations were recorded before the styrene transition at 10°C , with maximum E' values of 0.11 and 0.10 GPa for SBS-ibPOSS-blue 5 and SBS-ibPOSS-red 5, respectively. These results are indicative of the additional stiffness imparted by POSS. As filler content was increased past 5 wt%, the modulus began to decrease, suggesting that after a critical concentration (~ 5 wt%), POSS begins to lose reinforcing ability in this nanocomposites system. Filler agglomeration at higher concentrations reduces the particle surface area available to interact with the polymer, resulting in less-effective reinforcement. Zucchi *et al.* [40] attributed this reduction in elastic modulus to a decrease in the cohesive energy density caused by higher POSS concentrations. POSS functionalised with blue dye and containing isobutyl compatibilising groups exhibited the highest modulus values, attributed to the influence of dye structure and phase preference, respectively, on mechanical properties. This influence of dye-structure on mechanical properties is in agreement with behaviour observed in creep-recovery analysis. At temperatures above the polybutadiene transition, composites displayed higher E' values compared to pure SBS, while an increase in E' reduction rate was observed at temperatures above the polystyrene glass transition.

The loss modulus (E'') of SBS and nanocomposites is shown in Figure 12, while T_g values are sum-

Figure 12. Loss modulus (E'') curves across the polybutadiene glass-rubber transition of SBS and ibPOSS-filled composites

marised in Table 7. The T_g is determined by the peak of the E'' curve ($E''_{\max}$), since that is where maximum heat dissipation occurs. The curve of pure SBS displays two peaks, at -75 and 88°C . These peaks correspond to the T_g of the butadiene and styrene phases, respectively. Addition of POSS caused the T_g to increase in both phases, reaching a maximum at 5 wt%, before decreasing at higher concentrations. The initial increase in glass transition temperature is attributed to the ability of the functionalised-POSS to restrict molecular relaxation motions and bond rotations of the polymer chains. The decrease in loss (and storage) modulus at higher POSS concentrations has been observed previously [7, 35] and suggests that POSS exhibits a plasticising effect at sufficiently high levels. POSS agglomeration at concentrations greater than 5 wt% is also believed to be responsible for the decrease in moduli and T_g , as suggested by Kim *et al.* [35].

As displayed in Table 7, composites containing isobutylPOSS displayed the greatest increase in T_g for the butadiene phase, with ibPOSS-blue 5 and

ibPOSS-red 5 yielding T_g values of -70 and -71°C , respectively. Similarly, materials filled with phenyl-POSS exhibited higher T_g values in the styrene phase than their isobutylPOSS counterparts. This behaviour suggests that the compatibilising groups are providing an affinity for their corresponding phases, allowing the POSS to disperse throughout and entangle within a particular phase within the SBS. Despite being dispersed throughout the rubbery phase, isobutylPOSS increased the styrene phase T_g at concentrations up to 5 wt%, before decreasing with additional POSS content. Fu *et al.* [18] observed similar results, attributing the behaviour to an equal distribution of stress across both domains at temperatures near the styrene phase T_g ($\sim 88^\circ\text{C}$). This arises from the similar behaviour of the butadiene and styrene phases at this temperature, allowing the POSS molecules to act as physical crosslinks and reduce segmental relaxation. PhenylPOSS showed a similar, although less intense influence over the butadiene phase.

Nanocomposites functionalised with CI Reactive Blue 4 displayed slightly higher T_g values than those treated with CI Reactive Red 2. This was due to the bulkier structure of the blue-dye chromophore which allows for additional restraints on molecular motions. Nanocomposites exhibited glass transitions over a larger temperature range, as indicated by the broader E'' peaks. The increase in peak breadth is attributed to an increase in the segmental relaxation times of the matrix [41]. Peak breadth was observed to increase with POSS concentration, reaching maximum values at loadings of 10 and 20 wt%, suggesting an increase in the relaxation time due to segmental constraints, including polymer chain coupling and polymer-POSS interactions.

Table 7. Glass transition data of SBS and selected nanocomposites

Material	T_g from $E'_{\max}$ [$^\circ\text{C}$]		T_g from $\tan \delta_{\max}$ [$^\circ\text{C}$]		E' [MPa]	
	α	β	α	β	-90°C	10°C
SBS	-75	88	-67	95	2.0	0.03
ibPOSS-blue 5	-70	89	-62	94	3.1	0.11
ibPOSS-blue 20	-73	85	-64	97	2.6	0.04
ibPOSS-red 5	-71	88	-63	93	2.8	0.10
ibPOSS-red 20	-72	86	-64	90	2.4	0.05
phPOSS-blue 5	-73	93	-65	99	2.5	0.05
phPOSS-blue 20	-76	90	-68	97	2.2	0.04
phPOSS-red 5	-73	92	-66	98	2.3	0.04
phPOSS-red20	-76	91	-69	98	2.2	0.04

Figure 13. Loss tangent ($\tan\delta$) of SBS and 5 wt% filled composites

The loss tangent ($\tan\delta$) of SBS and several nanocomposites is shown in Figure 13. The maximum of the $\tan\delta$ curve can be used to determine T_g , although the E'' maximum is shown to be more consistent with other determinations of T_g . The $\tan\delta$ were ~ 6 – 9°C higher than T_g obtained from loss modulus curves (refer Table 6). The glass transition temperatures obtained from the loss tangent maximum displayed similar trends to those obtained from E''_{max} . Nanocomposites containing isobutylPOSS showed a reduction in butadiene-phase peak height, with 5 wt% exhibiting the greatest reduction. At concentrations above 5 wt%, the peaks began to increase towards the initial location of SBS. Conversely, the addition of isobutylPOSS caused an increase in the styrene-phase peak, reaching a maximum at 5 wt% before reducing at higher loadings. The amplitude of the $\tan\delta$ peak provides an indication of the number of kinetic units mobile enough to contribute to the glass transition [42]. The decrease in peak intensity indicates that isobutylPOSS molecules restrict motions of polymer chains within the butadiene phase, as indicated by the isobutylPOSS nanocomposites displaying T_g values higher than SBS. The increase peak height of the styrene phase indicates isobutylPOSS exerts a plasticising effect on the glassy domains, leading to composites displaying similar or lower T_g values than SBS. PhenylPOSS-blue nanocomposites experienced an increase in styrene-phase peak intensity, while a decrease was observed in phenylPOSS-red nanocomposites. This was particularly interesting since the blue-functionalised materials exhibited the greatest increase in T_g , which is usually characterised by a reduction in $\tan\delta$ peak intensity. The damping ability of a filled

polymer system is believed to be influenced by two factors; (a) the amount of free volume, (b) internal friction between the filler and matrix and between the filler particles themselves across the glass transition region [43]. The latter increases as the number of chain movements become greater, leading to an increase in damping ability. PhenylPOSS functionalised with bulkier CI Reactive Blue 4 experienced a greater amount of internal friction within the SBS matrix than its CI Reactive Red 2 counterpart, resulting in greater damping ability and internal friction.

The addition of phenylPOSS caused no increase in the butadiene-phase peak, which was expected since the styrene domains within SBS provide the polymer with rigidity and structure. As with the E'' curves, peak broadening of the $\tan\delta$ curves was observed at higher filler loadings. Since the peak breadth is an indication of structural heterogeneity (β parameter in KWW equation), the wider peaks suggest an increase in segmental relaxation time due to increased SBS-POSS interactions. The broader peaks are also indicative of the aforementioned increase in damping and internal friction.

4. Conclusions

POSS molecules were successfully functionalised with dichlorotriazine reactive dyes as indicated by FTIR and incorporated into SBS via physical blending. Agglomerate size and frequency increased with filler content, due to increased inter-POSS and inter-chromophore interactions. The morphology of the nanocomposites was dependent on the R groups on the POSS cages, with the amount of filler agglomeration being dependent on the relative volume of butadiene or styrene phase to disperse throughout. Colour intensity was able to be controlled by altering the functionalised POSS concentration. Films displayed uniform and smooth colour distribution at concentrations up to and including 5 wt%. Higher filler loadings resulted in colour swirling and fleck formation, due to increased filler diameters. Functionalised isobutylPOSS provided the greatest uniformity of colour, due to the greater amount of polymer (polybutadiene phase) which the POSS can be dispersed throughout. The use of dye-functionalised POSS as a pigment displayed limited success; at concentrations greater than 5 wt% surface treatment of the chromophore or further

processing (shear, greater ultrasonication, etc) are required to prevent filler agglomeration.

The thermal stability of SBS was enhanced by the addition of functionalised POSS. IsobutylPOSS had the greatest influence on thermal stability, due to its incorporation into the thermally-sensitive polybutadiene phase. POSS functionalised with CI Reactive Blue 4 exhibited a marginally better influence on thermal stability than its CI Reactive Red 2 counterpart, due to the thermal stability of the anthracene-based chromophore of CI Reactive Blue 4. The tensile modulus (E) of the nanocomposites increased with filler content, reaching a maximum at 5 wt%. Creep deformation decreased and permanent strain increased with POSS content, due to the restricted molecular motions caused by filler. Incorporation of POSS increased the storage modulus (E'), loss modulus (E'') and glass transition temperature (T_g), all reaching maximum values at filler concentrations of 5 wt%. The decrease in mechanical properties at POSS concentrations above 5 wt% was attributed to a disruption of the polymer molecular structure due to excess filler loading and reduction in material density. Three factors contributed to the mechanical properties of the nanocomposites; (a) POSS concentration, (b) the phase which the POSS was dispersed throughout, (c) chemical structure of the dye. The optimal POSS concentration was deemed to be 5 wt%.

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