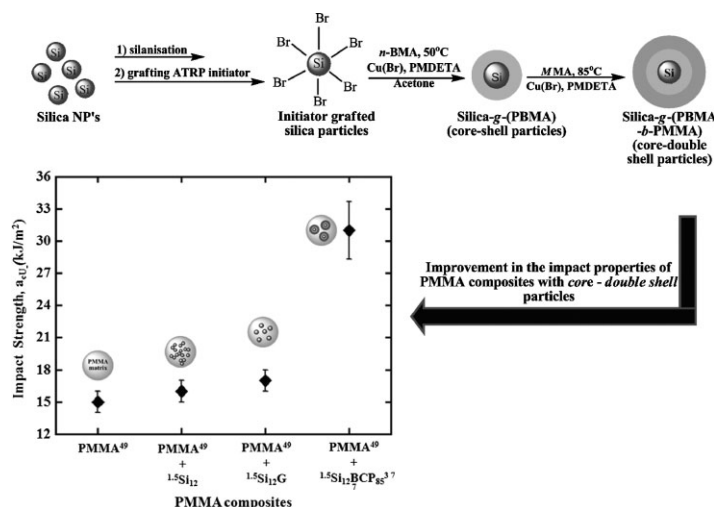


# Effect of Silica-Coated Poly(butyl methacrylate)-*block*-poly(methyl methacrylate) Double-Shell Particles on the Mechanical Properties of PMMA Composites

Golda Louis Chakkalakal, Michaël Alexandre, Adriana Boschetti-de-Fierro, Volker Abetz\*

Silica nanoparticles with an average diameter of 12 nm are grafted with PBMA-*b*-PMMA *double shells* through typical sequential ATRP from bromoisobutyrate initiators anchored at the silica surface using an epoxysilane. A commercially available PMMA homopolymer is used for the preparation of composites with unmodified, silane-modified and *double-shell*-modified silica particles. Good mechanical properties are obtained for silica *double shell* containing systems. The silica content in *double shell* particle systems is varied from 0 to 2.5 wt%. A significant improvement in impact properties is observed. The surface-modified silica particles are characterized by ATR-FTIR, NMR, GPC, and thermal analyses. TEM analysis is used to analyze the nature of dispersion of particles in the composites.



## 1. Introduction

The outstanding optical properties, weather resistance, and good mechanical strength made poly(methyl methacrylate) (PMMA) a widely used commodity plastic since a long time. However, its brittleness manifests itself as a limiting factor for being used in a very broad field of applications. The classical method for improving the toughness of a polymer matrix is achieved by incorporating discrete amount of rubbery-like modifier particles<sup>[1,2]</sup> and the second way is through the addition of modified or unmodified inorganic nanofillers.<sup>[3,4]</sup>

Emulsion polymerization and mechanical blending are the two common methods adopted for the preparation of

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rubber-toughened polymer composites.<sup>[5,6]</sup> An efficient stress transfer between the modifier phases and the matrix is necessary for an efficient toughening mechanism. For this, the rubbery phase needs to adhere to the matrix. Generally, this is achieved through a core-shell particle structure. It can be either (i) elastomeric core/external shell (single shell) or (ii) glassy core/elastomeric shell/external shell (double shell), which promotes good adhesion and reduces agglomeration.<sup>[7]</sup> The glassy core can be any glassy polymer depending on the nature of matrix used for the studies.

Secondly, the strengthening effects of inorganic nanoparticles in the polymer matrix can be effective only when the particles are well dispersed. However, the typical filler contents needed for such an enhancement of performance are as high as 20% by volume. The high particle loading leads to agglomeration of particles in the polymer matrix, thereby depreciates the processability of polymer, the final weight of the composites and their application in industry, especially in the field of electrical and electronic products. Sometimes, the resulting polymer matrix with nanoparticles exhibits properties even worse than conventional particle/polymer systems. Published works reported that considerable improvement in mechanical properties can be achieved at very low volume contents of nanosized fillers in the range 1–5 vol%.<sup>[8–11]</sup> Here arises the necessity of surface modification of particles.

As known, silica particles have been used as fillers to improve the mechanical properties of homo or copolymers.<sup>[12]</sup> Mechanical properties of PMMA composites added with surface modified silica nanoparticles have been reported.<sup>[13]</sup> The results showed some improvement in mechanical properties of PMMA composites with surface-modified particles. However, PMMA composites with silica core modified by block copolymer double shell particles having an elastomeric block (*inner shell*) for the property enhancement have not been reported yet.

Here we adopted the “grafting from” approach for the synthesis of poly(butyl methacrylate) (PBMA)-*block*-poly(methyl methacrylate) (PMMA) block copolymer (double shell) from silica particles using the well-known atom-transfer radical polymerization (ATRP).<sup>[14–17]</sup> The primary purpose of the outer PMMA shell is to enhance the dispersion of double shell particles in a PMMA matrix.

Hence, in the present context, the Si<sub>12</sub> particles were chosen for surface modification with double shell of block copolymers. Synthesis of PBMA grafted silica particles [Si<sub>12</sub>-*g*-(PBMA)Br, macroinitiator] and further synthesis of PMMA as a second block was performed on the basis of reported ATRP methods.<sup>[18,19]</sup> Epoxy silane was used to anchor ATRP initiator.<sup>[20]</sup> For the first time, here we tried to synthesize and investigate the effect of core/double shell particle containing an elastomeric inner shell on the mechanical properties of PMMA composites for low wt%

of silica content. The lower glass transition temperature ( $T_g$ ) value of PBMA made this polymer a suitable candidate for introduction of flexibility between the hard silica particle and the glassy PMMA matrix. In this work we explore its ability and influence of (co) polymer hybrid particles on properties and nature of dispersion in composites.

## 2. Experimental Section

### 2.1. Materials

Methyl methacrylate (MMA) and butyl methacrylate (*n*-BMA) were purified by passing through basic aluminum oxide (Aldrich) column to remove the antioxidant/inhibitor and stored at  $-5\text{ }^\circ\text{C}$  for later polymerization reactions. 3-Glycidoxypropyltrimethoxysilane (GPS) (>98%), triethylamine, 2-bromoisobutylbromide (2-BriB, 98%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), acetone (>99%), hydrofluoric acid (HF, 48 wt%), Aliquot 336, ethyl-2-bromoisobutyrate (2-EBriB, 98%) copper(I)bromide (99.99%, stored under vacuum) were used as received from Aldrich Chemicals. A colloidal silica suspension in water (Ludox-HS, 40 wt%) with an effective mean diameter of 12 nm (Si<sub>12</sub>, specific area =  $220\text{ m}^2\cdot\text{g}^{-1}$ , 4.7 OH groups per nm<sup>2</sup>) was provided from Aldrich Chemicals and used as received. PMMA (Plexiglas 6N glassklar) homopolymer ( $\bar{M}_n = 49\,000\text{ g}\cdot\text{mol}^{-1}$ ,  $\bar{M}_w = 89\,000\text{ g}\cdot\text{mol}^{-1}$ ,  $\bar{M}_w/\bar{M}_n = 1.8$ ) used for composite preparation was provided by Evonik Industries.

### 2.2. Characterization

Number-average molar mass ( $\bar{M}_n$ ), weight-average molar mass ( $\bar{M}_w$ ), and molar mass distribution ( $\bar{M}_w/\bar{M}_n$ ) were determined using gel permeation chromatography (GPC) in tetrahydrofuran (THF) at  $30\text{ }^\circ\text{C}$  with a flow rate of  $1\text{ mL}\cdot\text{min}^{-1}$ . Experiments were performed on a Waters instrument. The system is using 4 PSS SDV gel columns [ $10^2$ ,  $10^3$ ,  $10^4$ ,  $10^5\text{ \AA}$ , 8 mm (internal diameter)  $\times$  300 mm (length), PSS GmbH, Mainz, Germany]. PMMA standards were used for calibration.

Morphology of ultrathin sections of nanocomposites was analyzed by TEM. TEM observations were performed with a Tecnai G2 F20 electron microscope from FEI, using an accelerating voltage of 200 kV.

Characterization by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FT-IR) was made with a Bruker Equinox 55 after 32 scans at a spectral resolution of  $1\text{ cm}^{-1}$  under nitrogen atmosphere using a ZnSe ATR crystal set at  $45^\circ$ . The resulting single-beam spectra were ranged from 4000 to  $600\text{ cm}^{-1}$ .

<sup>1</sup>H NMR using the solvent (CDCl<sub>3</sub>) peak as a reference, solid-state <sup>13</sup>C CP/MAS, and <sup>29</sup>Si CP/MAS NMR were carried out on a Bruker AV-300 FT-NMR spectrometer at 300 MHz.

Thermal gravimetric analysis (TGA) measurements were carried out on a Netzsch TG209 F1 Iris. The experiments were conducted under a constant nitrogen flow ( $20\text{ mL}\cdot\text{min}^{-1}$ ), from 25 to  $900\text{ }^\circ\text{C}$ , at a constant rate of  $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ .

Differential scanning calorimetry (DSC) experiments were performed using a Netzsch DSC Phoenix. The samples were first heated to  $180\text{ }^\circ\text{C}$ , held for 3 min, cooled down to  $0\text{ }^\circ\text{C}$ , held for another 5 min, and finally heated to  $180\text{ }^\circ\text{C}$ . All the measurements

were done under nitrogen atmosphere at a constant rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .

The strain/stress experiments were carried out on a Zwick model Z020, with a load cell of 20 kN. The measurements were done with a crosshead speed of  $1\text{ mm}\cdot\text{min}^{-1}$  at ambient temperature, according to the standard ASTM D882. The samples were prepared according to ISO 527-2B standard.

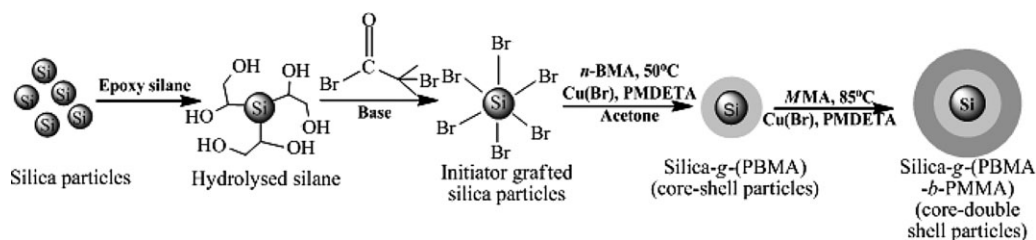
The impact measurements were carried out using a Charpy impact tester from Zwick model Hit 25 P. Specimens were prepared according to ISO 179 standards. Un-notched specimens with rectangular dimensions of  $80\times 10\times 4\text{ mm}^3$  were fractured at 4 J with an impact speed of  $2.9\text{ m}\cdot\text{s}^{-1}$  at ambient temperature. The distance between the support span was kept constant to 62 mm.

### 2.3. Surface Modification of Silica by Epoxysilane Followed by Anchoring ATRP Initiator<sup>[21]</sup>

A colloidal suspension of silica particles (12 g) was refluxed with GPS (0.05 mol, 12 mL) for 24 h. The resultant silane-grafted silica particles was precipitated in methanol and centrifuged three to four times. The centrifugate was then redispersed in THF. The amount of coupled silane was evaluated by TGA. The amount of THF in the final solution was adjusted to have a concentration of silanized silica not larger than  $0.065\text{ g}\cdot\text{mL}^{-1}$  and sonicated for 15 min. The dispersion in THF was subjected to bromination with 2-BriB (0.009 mol, 1.1 mL) in the presence of triethylamine at room temperature. Then the reaction mixture was washed by centrifugation with methanol three to four times to remove excess bromide and dried in a vacuum oven. The success of functionalization reactions was verified through spectral characterization.

### 2.4. Synthesis of $\text{Si}_{12}\text{-g-(PBMA)Br}$ Macroinitiator

Silica colloidal initiator (500.0 mg, 0.18 mmol of ATRP initiator) and  $\text{Cu(I)Br}$  (0.025 g, 0.18 mmol) were added to a round bottom flask and degassed and back-filled with nitrogen. Deoxygenated acetone (6 mL) was added to the flask followed by *n*-BMA (7 mL, 0.045 mol) under nitrogen atmosphere. The solution was magnetically stirred in order to dissolve the metal complex as well as to disperse the colloidal initiator. Finally the ligand, PMDETA (37  $\mu\text{L}$ , 0.18 mmol) was added. The reaction mixture was placed in a previously heated oil bath at  $50\text{ }^{\circ}\text{C}$ . After reaction, the reaction mixture was precipitated in 6:1 ratio of methanol and water, filtered and dried. The resultant grafted polymer was cleaved from silica after treatment with HF and Aliquot 336 for GPC analysis.<sup>[22]</sup>



■ Scheme 1. General scheme of reactions for grafting ATRP initiator followed by PBMA/PMMA on silica particles.

### 2.5. Synthesis of $\text{Si}_{12}\text{-g-(PBMA-b-PMMA)}$ Block Copolymer from $\text{Si}_{12}\text{-g-(PBMA)Br}$ Macroinitiator

$\text{Si}_{12}\text{-g-(PBMA)Br}$  hybrid nanoparticles (500 mg, 0.05 mmol),  $\text{Cu(I)Br}$  (0.0072 g, 0.05 mmol) were added to a round-bottom flask. It was degassed and backfilled with nitrogen. MMA (6 mL, 0.056 mol) was added to the flask under nitrogen atmosphere with stirring. PMDETA (10.4  $\mu\text{L}$ , 0.05 mmol) was added to the reaction flask and then transferred to a previously heated ( $85\text{ }^{\circ}\text{C}$ ) oil bath. After reaction, the reaction mixture was precipitated in 4:1 ratio of methanol and water, filtered and dried. The resultant grafted block copolymer was cleaved from silica after treatment with HF for GPC analysis.

### 2.6. Preparation of Composites

PMMA (matrix) polymer was dissolved in chloroform, to which the desired amount of (co)polymer-grafted silica particles (with respect to silica content) was added and magnetically stirred for 24 h and then sonicated (Elma S3OH, Elmasonic) for 10–15 min. The dispersion was then cast to a film on a Teflon/glass plate and kept for 2–3 d at room temperature (RT). The resultant film was dried in vacuum oven at RT for 24 h followed by heating at  $40\text{ }^{\circ}\text{C}$  for 48 h. The small stripes of the above films were compounded in the miniextruder (Micro 15cc Twin Screw Compounder, DSM Xplore Netherlands) at  $210\text{ }^{\circ}\text{C}$  under nitrogen atmosphere. The resultant specimens were subjected to tensile and impact measurements.

## 3. Results and Discussion

### 3.1. Characterization of Functionalized Silica Particles

The grafting of the ATRP initiator onto the silica nanoparticles was performed in two steps (see Scheme 1). The silica particles used were initially dispersed in a basic aqueous suspension. The first step involved the silanization of the particles with an epoxy silane. The second step consisted in the esterification of the vicinal hydroxyl groups (diol obtained after epoxy hydrolysis) with 2-bromoisobutryl bromide.

The quantitative measurements of coupled silane were carried out through TGA analysis on samples dried at a temperature of  $100\text{ }^{\circ}\text{C}$  for 18 h. For 2.5 equiv. of epoxy silane, GPS coupled on  $\text{Si}_{12}$  particles (having surface area  $220\text{ m}^2\cdot\text{g}^{-1}$ ) was 10 wt% ( $\approx 2\text{ GPS}\cdot\text{nm}^{-2}$ ) under controlled

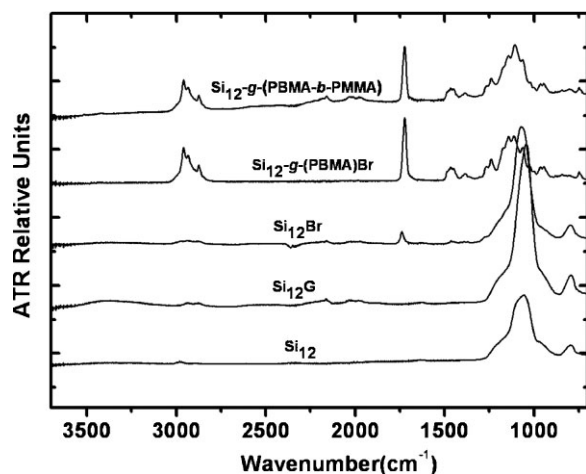


Figure 1. ATR-FTIR spectra of pristine silica particles ( $\text{Si}_{12}$ ), silica particles after coupling with epoxy silane ( $\text{Si}_{12}\text{G}$ ), initiator-grafted silica ( $\text{Si}_{12}\text{Br}$ ), PBMA-modified silica particles ( $\text{Si}_{12}\text{-g-(PBMA)Br}$ ), and block-copolymer-grafted silica particles ( $\text{Si}_{12}\text{-g-(PBMA-b-PMMA)}$ ).

reaction conditions. ATR-FTIR spectroscopy was carried out to account for the success of the grafting reactions (shown in Figure 1). The peak around  $1045\text{--}1053\text{ cm}^{-1}$  comes from the typical Si–O–Si stretching vibration from silica particles. After silanization (see Figure 1,  $\text{Si}_{12}\text{G}$ ), the peak at around  $2940\text{ cm}^{-1}$  is characteristic of the C–H stretching vibration of the methylene group in the organic moiety. TGA analysis shows a bromide concentration of  $0.36\text{ mmol}\cdot\text{g}^{-1}$  after grafting ATRP initiator onto silanized particles. The sharp absorption band near  $1740\text{ cm}^{-1}$  (see Figure 1,  $\text{Si}_{12}\text{Br}$ ) comes from the C=O stretching vibration after the esterification by the ATRP initiator. The broad stretching band near  $3400\text{--}3450\text{ cm}^{-1}$  corresponds to the –OH groups from the silica or from the hydrolyzed epoxy groups. On the basis of the above results obtained after initiator grafting we concluded that the epoxy group got transformed into functional diol. The analysis of  $^{13}\text{C}$  spectra (shown in Figure 2) in solid phase was carried out in order to confirm that epoxy silane immobilized on silica undergoes ring opening reactions. A peak was observed at  $\delta = 63\text{ ppm}$ , which corresponds to the characteristic primary alcohol and the one at  $\delta = 70\text{ ppm}$  corresponds to the secondary alcohol (together with  $-\text{CH}_2$ 's in  $\alpha$  of the ether group).

### 3.2. Synthesis and Characterization of Block Copolymer Hybrid Silica Particles

The detailed synthesis of silica nanoparticles grafted with PBMA macroinitiator,  $\text{Si}_{12}\text{-g-(PBMA)Br}$ , followed by the synthesis of PMMA outer block was described in Section 2. PBMA-grafted silica particles were synthesized from silica colloidal initiators under the condition,  $[\text{n-BMA}]:[\text{Si}_{12}\text{Br}]:[\text{Cu(I)Br}]:[\text{PMDETA}] = 250:1:1:1$  at  $50\text{ }^\circ\text{C}$ . The

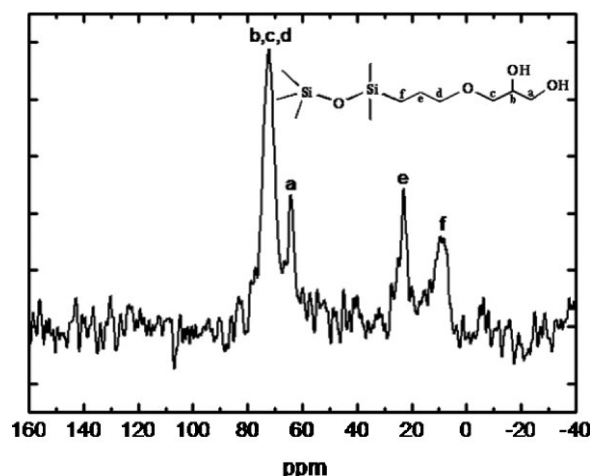


Figure 2. Solid state  $^{13}\text{C}$  CP/MAS spectrum of  $\text{Si}_{12}$  silica particles coupled with hydrolyzed epoxy silane.

reaction was carried out in acetone as solvent. After the reaction, PBMA with a molar mass of  $26\,000\text{ g}\cdot\text{mol}^{-1}$  and a polydispersity index (PDI) of 1.3 was obtained after degrafting reaction from silica particles. TGA analysis showed a weight fraction of 70 wt% of PBMA on the  $\text{Si}_{12}$  particles (represented by  $\text{Si}_{12}\text{PBMA}_{70}^{26}$ ). The second block (outer shell) of PMMA was synthesized from the PBMA macroinitiator with a bromide concentration  $0.05\text{ mmol}\cdot\text{g}^{-1}$ . The molar ratios are  $[\text{MMA}]:[\text{Si}_{12}\text{PBMA}_{70}^{26}\text{-Br}]:[\text{CuBr}]:[\text{PMDETA}] = 1100:1:1:1$ . The reaction was carried out at  $85\text{ }^\circ\text{C}$ . The resultant molar mass of the degrafted block copolymer was  $37\,000\text{ g}\cdot\text{mol}^{-1}$  (represented by  $\text{Si}_{12}\text{BCP}_{85}^{37}$ ) where BCP stands for block copolymer, the superscript represents its molar mass in  $\text{kg}\cdot\text{mol}^{-1}$  and the subscript the weight fraction of BCP in the double-shell modified silica nanoparticles with a PDI of 1.34. The molar fraction of the PBMA block calculated from  $^1\text{H}$  NMR was found to be 0.56. The TGA analysis of block copolymer hybrid silica particles shows a weight fraction of 85% ( $\text{Si}_{12}\text{BCP}_{85}^{37}$ ). The GPC curves of degrafted PBMA and PBMA-*b*-PMMA chains are shown in Figure 3.

The yield of the final product was low because of the low efficiency of  $\text{Si}_{12}\text{-g-(PBMA)Br}$  macroinitiator to initiate PMMA polymerization.  $^1\text{H}$  NMR spectra (see Figure 4) was used to complete the characterization of the grafted block copolymer. Figure 4 presents the  $^1\text{H}$  NMR spectra of (i) pure PMMA, (ii)  $\text{Si}_{12}\text{PBMA}_{70}^{26}\text{-Br}$  macroinitiator, (iii) block-copolymer-grafted silica particles,  $\text{Si}_{12}\text{-g-(PBMA-b-PMMA)}_{85}^{37}$ .

The  $^1\text{H}$  NMR spectra allow the determination of the molar composition from the relative intensity of the resonance signals at  $\delta = 4$  ( $-\text{OCH}_2$  protons of the butyloxy group) for butyl methacrylate (*n*-BMA) and at  $\delta = 3.6$  ( $-\text{OCH}_3$  protons of the methyloxy group) for methyl methacrylate. In the FTIR-ATR analysis (see Figure 1), the intensity of carbonyl ( $-\text{C}=\text{O}$ ) stretching band near  $1750\text{ cm}^{-1}$  for initiator

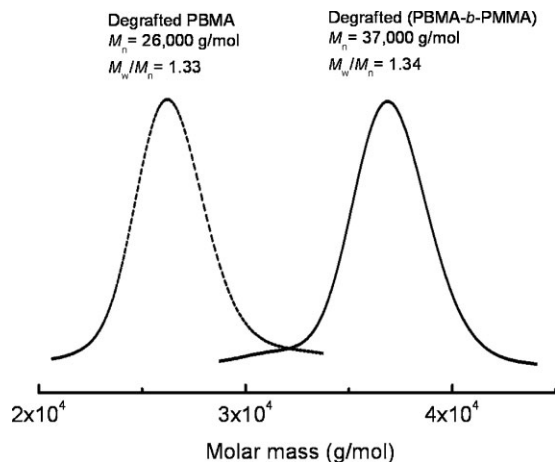


Figure 3. GPC curves of degrafted PBMA and PBMA-*b*-PMMA (co)polymer chains from silica particles, Si<sub>12</sub>-*g*-(PBMA)<sup>26</sup> and Si<sub>12</sub>-*g*-(PBMA-*b*-PMMA)<sup>37</sup>, respectively.

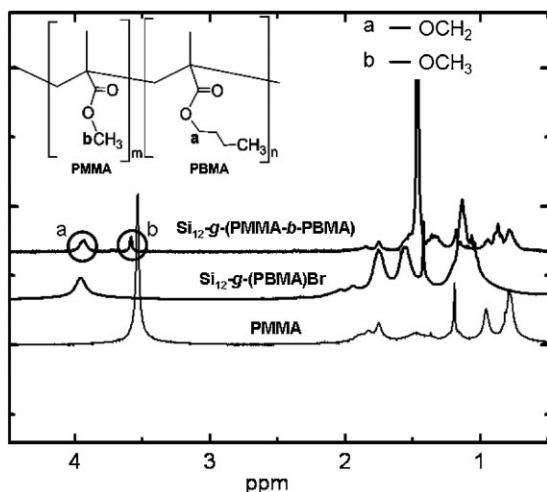


Figure 4. <sup>1</sup>H NMR spectra of (i) pure PMMA, (ii) Si<sub>12</sub>PBMA<sub>70</sub><sup>26</sup>-Br macroinitiator, (iii) block copolymer grafted silica particles, Si<sub>12</sub>-*g*-(PBMA-*b*-PMMA)<sup>37</sup>.

anchored silica particles (Si<sub>12</sub>Br) increases sharply after each step of grafting Si<sub>12</sub>PBMA<sub>70</sub><sup>26</sup>-Br and Si<sub>12</sub>-*g*-(PBMA-*b*-PMMA)<sup>37</sup>, coming from the ester moiety of the (co)polymer. Moreover, the antisymmetric C–O–C stretching mode in esters gives rise to a very strong and broad band around the region, 1430–1460 cm<sup>-1</sup>.

The phase study of diblock copolymer grafted silica nanoparticles was carried out by measuring the glass transition temperatures (*T*<sub>g</sub>'s) by differential scanning calorimetry (DSC). After grafting the PBMA shell on silica nanoparticles (Si<sub>12</sub>PBMA<sub>70</sub><sup>26</sup>), the *T*<sub>g</sub> value raises to 47 ± 3 °C. An equivalent free PBMA homopolymer ( $\bar{M}_n = 27\,450 \text{ g} \cdot \text{mol}^{-1}$  and  $\bar{M}_w/\bar{M}_n = 1.32$ ) was synthesized (as a reference) via ATRP using the initiator ethyl-2-bromoiso-butyrate under similar reaction conditions showed a *T*<sub>g</sub>

value of 23 ± 2 °C. The increase in *T*<sub>g</sub> value of PBMA grafted silica particles arises due to the decrease in the mobility of polymer chains through the covalent bond (strong interaction) between silica nanoparticles and the grafted polymer. After grafting the outer PMMA shell, Si<sub>12</sub>-*g*-(PBMA-*b*-PMMA)<sup>37</sup>, the *T*<sub>g</sub> value of PMMA block was observed near 96 ± 3 °C. This proves the successful grafting reaction of block copolymer on silica nanoparticles.

### 3.3. Tensile, Impact, and Morphological Characterization of PMMA Composites with Silica-*g*-(PBMA-*b*-PMMA) (Core/Double Shell) Particles

The composites for mechanical and morphological characterization were prepared by the procedure described in Section 2. Even though studies reported that an improvement in tensile and impact properties of PMMA composites is achievable by the addition of pristine, silane modified or polymer modified silica nanoparticles at small loadings,<sup>[12,13]</sup> the improvement in properties is not significant when we compare them with the latest reported values obtained from a rubber toughened PMMA matrix.<sup>[23]</sup> In the present work, we investigate how silica core-double shell particles of defined molar mass, elastomeric content, and core size can affect the tensile, impact, and morphological properties of PMMA composites. PMMA composites of core-double shell particles were prepared with silica content varying in between 0 and 2.5 wt%. Optimum tensile and impact properties were observed at 1.5 wt%. The value of impact strength (106%) was found to improve significantly. Similarly, elongation at break, modulus of elasticity, and tensile strength were also found to increase by 40, 26, and 12%, respectively. Figure 5(a and b) describe the variation in tensile and impact properties of PMMA composites by varying amounts of core-double shell particles.

Recent studies of Suu reported that unnotched specimen of PMMA composite achieved nearly 43% improvement in impact strength for 7.5 wt% PMMA-modified natural rubber (MNR).<sup>[23]</sup> Also, the optimum increment in tensile strength (17%) and elongation at break (41%) was achieved by the addition of 2.5 wt% of MNR.

In the present studies, the optimum mechanical properties of PMMA composites are achieved at a loading of 1.5 wt% of silica core-double shell particles. The enhancement in mechanical properties, especially impact strength, shows the efficiency of core-double shell particles.

Beyond 1.5 wt%, the values decrease but still the properties are better than either pure PMMA or those composites containing pristine and silane modified silica. In contrast to the classical three-layer core/shell (with a hard glassy polymer core) and two-layer (with a soft core) structures, silica nanoparticles are used as the inner core and PBMA as the inner shell with a PMMA outer shell in the present studies. The observed mechanical properties of

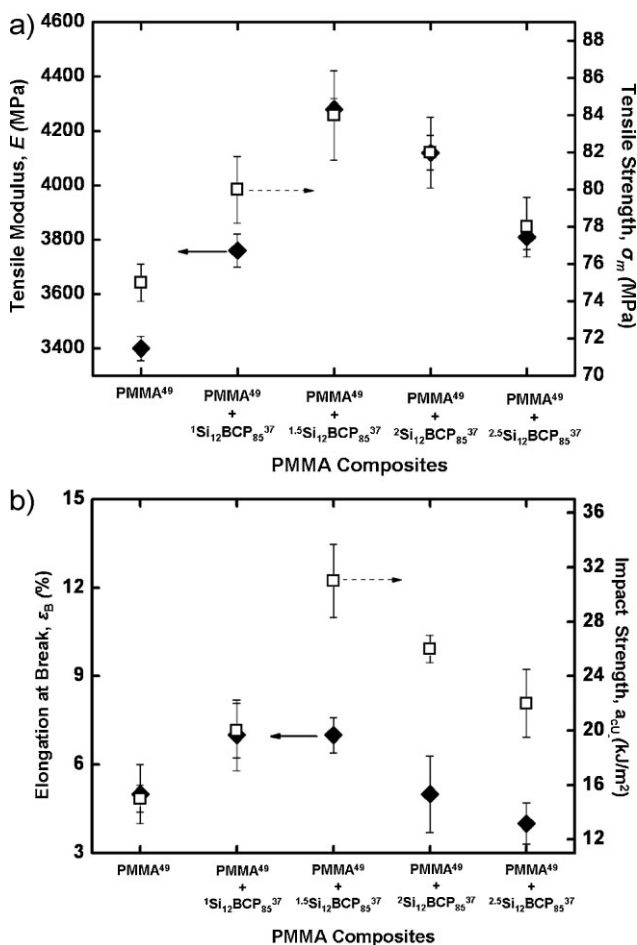


Figure 5. Variation of (a) tensile modulus and tensile strength and (b) elongation at break and impact strength of PMMA and its composites with 0–2.5 wt% loadings of silica core-double shell particles. The superscript 49 in PMMA<sup>49</sup> denotes the molecular weight of matrix PMMA in  $\text{kg} \cdot \text{mol}^{-1}$ .  $a\text{Si}_{12}\text{BCP}_y^{37}$ , the superscripts  $a$  and  $y$  correspond to the silica content in the composite in wt% and molecular weight of grafted block copolymer (BCP) in  $\text{kg} \cdot \text{mol}^{-1}$  respectively and the subscripts 12 and  $x$  for the average core diameter of silica nanoparticles in nm and weight fraction of grafted BCP measured from thermogravimetry measurements.

PMMA composites containing simply silica grafted PBMA particles ( $\text{Si}_{12}\text{PBMA}_{70}^{26}$ ) exhibits an improvement in properties for 2 wt% of silica content. The observed improvement in impact strength, tensile modulus, tensile strength, and elongation at break were 55, 15, 10, and 47%, respectively. Obviously these values are lower than those obtained by the addition of silica double shell particles at 1.5 wt%. These observations show that the outer PMMA shell of silica core/double shell particles indeed improves the dispersion in PMMA matrix and altogether improves the mechanical properties of the composites. The TEM image (see Figure 6) of ultrathin-cut of PMMA composite sample after impact measurement is shown below. One can observe small aggregates together with some isolated modified particles.

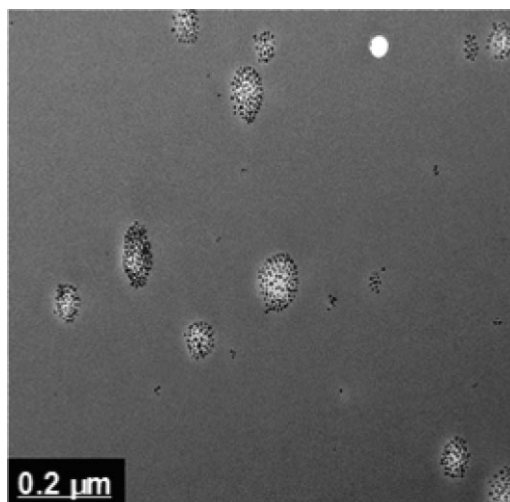


Figure 6. TEM image of ultrathin-cut of PMMA<sup>49</sup>- $1.5\text{Si}_{12}$ -g-(PBMA-b-PMMA)<sub>8537</sub> composite sample used for impact measurement having a net silica content of 1.5 wt%.

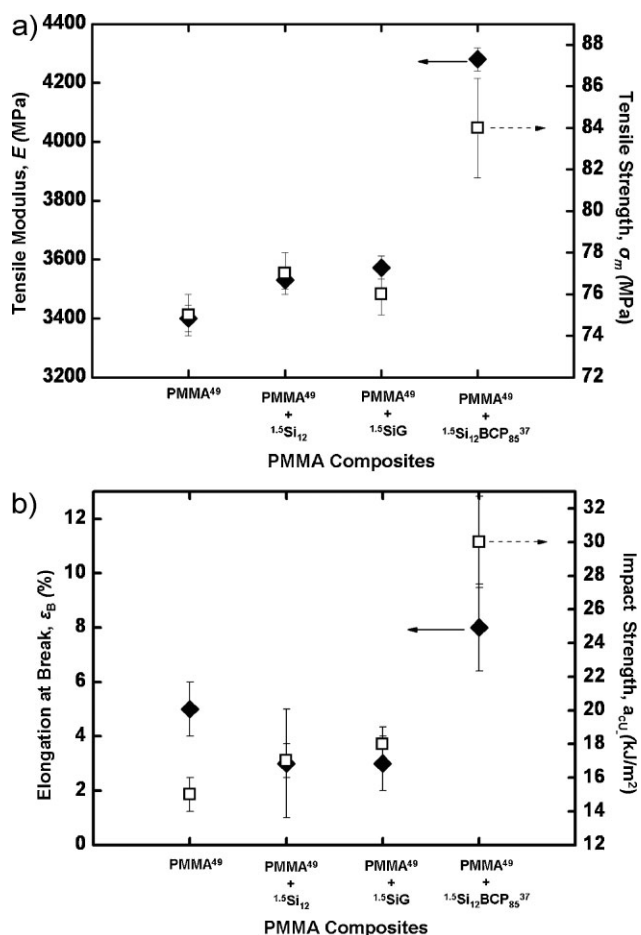


Figure 7. Optimum (a) tensile modulus and tensile strength and (b) elongation at break and impact strength of pure PMMA<sup>49</sup> and its composites obtained with Si<sub>12</sub> (PMMA<sup>49</sup> +  $1.5\text{Si}_{12}$ ), GPS grafted Si<sub>12</sub> (PMMA<sup>49</sup> +  $1.5\text{Si}_{12}\text{G}$ ), and BCP-grafted Si<sub>12</sub> (PMMA<sup>49</sup> +  $1.5\text{Si}_{12}\text{BCP}_{85}^{37}$ ) particles having a net silica content of 1.5 wt%.

These small aggregates might positively improve the mechanical properties of composites.

Apart from the present results, one could anticipate varying mechanical properties and dispersion of modified particles by varying the core size, weight fraction or graft density of PBMA inner block and outer PMMA shell and final size distribution of modified particles in polymer matrix. Following Figure 7(a and b) gives an overall impression of optimum mechanical properties of PMMA composites obtained with various surface modified Si<sub>12</sub> particles adopted in the present work for a net silica content of 1.5 wt%.

#### 4. Conclusion

PMMA composites exhibit a significant improvement in mechanical properties, especially the impact properties for lower loadings (1.5 wt%) of silica particles (Si<sub>12</sub>) grafted with PBMA-*b*-PMMA (double shell) block copolymer for a given graft molecular weight and size distribution. The observed improvement in impact properties with double shell particles is much better than other surface modified particles. These results open the door to use silica nanoparticles (of a given core size) grafted with polymeric shells (double shell in the present case) of desired characteristics to improve the mechanical properties of polymer composites.

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[1] H. Keskkula, *Rubber-Toughened Plastic*, American Chemical Society, New York **1989**, p. 289.

- [2] C. B. Bucknall, *Toughened Plastics*, Applied Science Publishers, London **1977**.
- [3] A. Savadori, M. Scapin, R. Walter, *Macromol. Symp.* **1996**, *108*, 1.
- [4] B. Pukanszky, "Particulate filled poly(propylene) composites", in: *Polypropylene: An A-Z Reference* (Ed., J. Karger-Kocsis), Kluwer Academic Publishers, Dordrecht **1999**, pp. 574–580.
- [5] J. Hooley, D. R. Moore, M. Whale, M. J. Williams, *Plastic Rubber Process. Appl.* **1981**, *1*, 45.
- [6] O. Mauzac, R. Schirrer, *J. Appl. Polym. Sci.* **1989**, *38*, 2289.
- [7] C. Wrottecki, P. Heim, P. Gaillard, *Polym. Eng. Sci.* **1991**, *31*, 213.
- [8] M. Z. Rong, M. Q. Zhang, Y. X. Zheng, H. M. Zeng, R. Walter, K. Friedrich, *J. Mater. Sci. Lett.* **2000**, *19*, 1159.
- [9] M. Q. Zhang, M. Z. Rong, S. L. Yu, B. Wetzels, K. Friedrich, *Macromol. Mater. Eng.* **2002**, *2*, 111.
- [10] T. Naganuma, Y. Kagawa, *Comp. Sci. Technol.* **2002**, *62*, 1187.
- [11] Y. P. Zheng, Y. Zheng, R. C. Ning, *Mater. Lett.* **2003**, *57*, 2940.
- [12] H. Zou, S. Wu, J. Shen, *Chem. Rev.* **2008**, *108*, 3893.
- [13] R. Y. Hong, H. P. Fu, Y. J. Zhang, L. Liu, J. Wang, H. Z. Li, Y. Zheng, *J. Appl. Polym. Sci.* **2007**, *105*, 2176.
- [14] O. Prucker, J. Ruhe, *Macromolecules* **1998**, *31*, 602.
- [15] T. E. Pattern, K. Matyjaszewski, *Adv. Mater.* **1998**, *10*, 901.
- [16] M. Alexandre, P. Dubois, in: *Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*, Eds., K. Matyjaszewski, Y. Gnanou, L. Leibler), Vol. 4, Chapter 2 Wiley - VCH, Weinheim **2007**, p. 2033.
- [17] R. Barbey, L. Lavanant, D. Paripovic, N. Schüwer, C. Sugnaux, S. Tugulu, H. A. Klok, *Chem. Rev.* **2009**, *109*, 5439.
- [18] K. A. Davis, K. Matyjaszewski, *Chin. J. Polym. Sci.* **2004**, *22*, 195.
- [19] M. Fernández-García, J. Luis De La Fuente, M. Fernández-Sanz, E. L. Madruga, *J. Appl. Polym. Sci.* **2002**, *84*, 2683.
- [20] S. Etienne, C. Becker, D. Ruch, B. Grignard, G. Cartigny, C. Detrembleur, C. Calberg, R. Jerome, *J. Therm. Anal. Calorim.* **2007**, *87*, 101.
- [21] G. L. Chakkalakal, M. Alexandre, C. Abetz, A. Boschetti-de-Fierro, V. Abetz, *Macromol. Chem. Phys.* in press, DOI: 10.1002/macp.201100625.
- [22] J. Pyun, S. Jia, T. Kowalewski, G. D. Patterson, K. Matyjaszewski, *Macromolecules* **2003**, *36*, 5094.
- [23] Y. G. Suu, Studies on Mechanical Properties of Poly(methyl methacrylate) and Poly(methyl methacrylate)-Modified Natural Rubber Blend, *Master Thesis*, Science University Malaysia 2008.