SYNTHESIS AND CHARACTERIZATION OF CHLORINE-FUNCTIONALIZED POLYSTYRENE NANOPARTICLES AS REACTIVE FILLER

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ABSTRACT

A convenient method of preparing ultrafine polystyrene latex nano-particles with chlorine groups on the surface is developed. Polystyrene latexes in the size range 50–400 nm were prepared via emulsion polymerization, using sodium dodecyl sulfate (SDS) as surfactant. The poly styrene with chlorine groups on the surface will be fine to use as organic filler to modify rubber. Transmission electron microscopy (TEM) was used to observe the morphology of silicon dioxide and functionalized polystyrene nanoparticles. The nature of bonding between the polymer and the reactive groups on the filler surfaces was analyzed using Fourier transform infrared spectroscopy (FTIR). Scanning electron microscopy (SEM) was employed to examine the filler surface.

Keywords:- *Emulsion polymerization, Reactive filler, Nano-particle.*

1. INTRODUCTION

In recent years, organic fillers have drawn attention as reinforcement in thermo- plastics. The advantages, compared with inorganic fillers, are their low-density, low abrasion, availability of renewable resources, low cost and no waste disposal problems. In spite of this, composites containing organic fillers are used in various applications as decks and docks, window frames, or, in the last years, also as materials in the automobile industry. A possible route to create reactive organic filler is the in the emulsion polymerization of a reactive filler for polymer material in the presence of organic or inorganic substances. The filler often used to modify the properties of rubber and plastic products and plays a significant role. The term “filler” is misleading, implying a material intended primarily to occupy space and act as a cheap diluents of the more costly elastomer. Most of the fillers used today offer some functional benefit that contributes to the process-ability or utility of the rubber or plastic product. The characteristics which determine the properties that filler will impart to a composite are particle shape, particle size, surface area and particle-matrix compatibility. Particle-matrix compatibility relates to the ability of the polymer to coat and adhere to the filler. For example, polypyrrole can coat the surface of conventional organic polymer powder particles such as polyethylene (PE), polypropylene (PP) [1, 2]' poly (vinyl chloride) [3, 4], polystyrene latexes [5], or inorganic colloids [6, 7], and nanoparticles such as multi-walled carbon nanotubes [8]. In this work we prepared and investigated a new type of organic reactive filler for polymer material which are based on polystyrene and chloromethylstyrene as reactive chlorine groups on the surface. Our aim was to obtain two types of organic reactive filler such as polystyrene with reactive chlorine groups on surface particles and silicon dioxide core covered with functionalized polystyrene particles with nano particle size to be used for modifying rubber which contain amino reactive groups.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

Styrene (St, monomer, Sigma-Aldrich) was distillated under reduced pressure before use. Chloromethylstyrene (CMS, functional monomer, Sigma-Aldrich, 90%, inhibited with 500 ppm tert-butylcatechol and 500 ppm nitroparaffin) and divinylbenzene (DVB, crosslinking monomer, Sigma-

Aldrich, 80%, inhibited with 1000 ppm tert-butylcatechol) were used as received. Potassium Peroxydisulfate (KPS, initiator) and azodiisobutyramidine dihydrochloride (AIBA, positively charged initiator) were purchased from Sigma-Aldrich and used as received. Ammonium persulfate (APS, initiator), sodium dodecylsulfonate (SDS, surfactant) and $NaHCO_3$ (buffering agent) were purchased from Beijing Chemical Works and were used without further purification. Nano-size SiO_2 aqueous dispersion (ca. 28wt% solid content) was kindly provided by Beijing Xing Da Xin Company.

3. PRACTICAL WORK

This part outlines the general experimental techniques and procedures used in this work. Specific experimental methods those are unique to particular studies will be described in the appropriate part. Synthesizing reactive filler with chlorine groups on the surface with nano/micro-particle size is the most important aim to be reached. Different reactive filler with chlorine groups on the surface, such as chloro-functionalized PSt, cross-linked chloro-functionalized PSt and organic–inorganic composite particles were prepared.

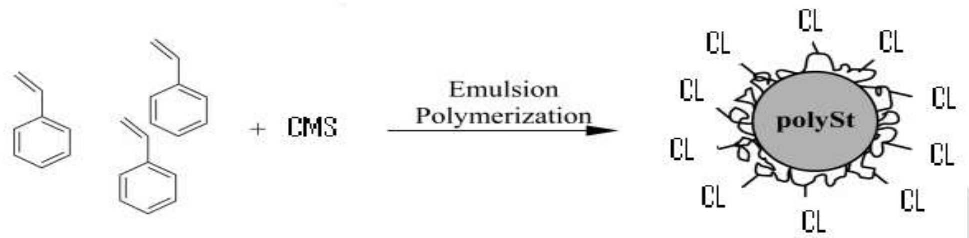

Figure 1. Schematic preparation of chloro-functionalized polystyrene

3.1 Synthesis of Chloro-functionalized Polystyrene (PS) Particles.

A typical recipe is as follows: St 63.00g, CMS 3.00g (5.0 wt % to St), SDS 0.55 g, KPS 2.50 g (dissolved in 40 g deionized water), $NaHCO_3$ 1.20 g and additional deionized water 480 g. A 1000 mL four-necked flask equipped with a mechanical stirrer, thermometer and condenser were used as the reactor. The reaction was carried out under nitrogen atmosphere in a water bath. The stirring rate was held constant at 300 rpm for the whole process. Both the surfactants, SDS and $NaHCO_3$, were introduced into the reaction flask containing deionized water at 40 °C. After stirring for 30 min, the temperature was raised to 89 °C. The solution of KPS and St were added. The polymerization proceeded at 89 °C for 6 h. Then, CMS was added drop-wise. After complete addition of CMS, the temperature was then decreased to 60°C. The polymerization was carried out for a further 18 h.

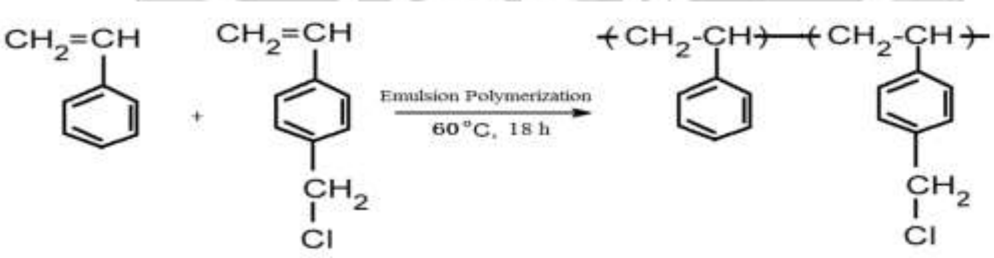

Figure 2. Synthesis of chloro-functionalized polystyrene particles

3.2 Synthesis of Crosslinked Chloro-functionalized Polystyrene Particles

A typical recipe is as follows: St 63.00g, DVB 1.00g, CMS 3.00g (5.0 wt % to St), SDS 1.00 g, KPS 2 g (dissolved in 40g deionized water), $NaHCO_3$ 1.20 g, and additional deionized water 490 g. A 1000 mL four-necked flask equipped with a mechanical stirrer, thermometer and condenser were used as the reactor. The reaction was carried out under nitrogen atmosphere in a water bath. The stirring rate was held constant at 300 rpm for the whole process. Both the surfactants, SDS and $NaHCO_3$, were introduced into the reaction flask containing deionized water at 40 °C. After stirring for 30 min, the temperature was raised to 89 °C. The solution of KPS, St and DVB were added. The polymerization proceeded at 89 °C for 6 h. Then, CMS was added drop-wise. After complete addition of CMS monomer, the temperature was then decreased to 60°C. The polymerization was carried out for a further 18 h.

3.3 Synthesis of Particles with Silicon dioxide Core Covered by Chloro-functionalized Polystyrene

Styrene (St) and negatively charged SiO_2 with mean diameter of 28 nm were used to prepare inorganic-organic composite filler particles via surfactant-free emulsion polymerization using positively charged initiator, AIBA. Typical process to prepare functionalized polystyrene coated SiO_2 filler particles was as follows: Deionized water (600 mL) was added to 1000-mL four necked round bottom flask equipped with a mechanical stirrer, a dropping funnel, and N_2-controlled equipment. The flask was then purged of air with bubbling nitrogen for 30 min at room temperature. SiO_2 (6.00g solid) and then an aqueous solution of AIBA were added. The temperature was increased to 80°C, and then the selected amount of St (1.60g) was added drop-wise with the stirring rate at about 330 rpm. The polymerization was carried out for 4h. The temperature was then declined to 60°C with stirring at about 370 rpm and CMS (1.60g) was added. The reaction continued for additional 18h to obtain organic–inorganic composite filler particles (as shown Figure 3).

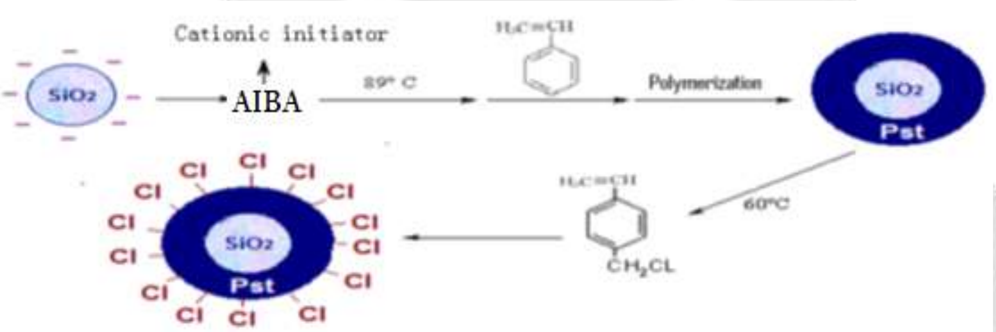

Figure 3. Schematic preparation of functional core/shell polymers

3.4. Synthesis of Particles with SiO_2 Core Covered by Crosslinked Chloro- functionalized PSt

Styrene (St) and negatively charged SiO_2 with mean diameter of 28 nm were used to prepare inorganic-organic composite filler particles via surfactant-free emulsion polymerization using positively charged initiator, AIBA. Typical process to prepare functionalized polystyrene coated SiO_2 filler particles was as follows: Deionized water (600 mL) was added to 1000-mL four necked round bottom flask equipped with a mechanical stirrer, a dropping funnel. The flask was then purged of air with bubbling nitrogen for 30 min at room temperature. SiO_2 (6.00g solid) and then aqueous solution of AIBA were added. The temperature was increased to 80°C, and then selected amount of St (1,00g) and DVB (0.02g) were added drop-wise with stirring at about 330 rpm. The polymerization was carried out for 6h. The temperature was then declined to 60°C with stirring at about 370 rpm and CMS (0.20g) was added drop-wise. The reaction continued for additional 18h to obtain organic–inorganic composite filler particles.

4. CHARACTERIZATION OF FUNCTIONAL POLYMERS

The degree of monomer to polymer conversion was determined gravimetrically following the procedure described by Lee [9] before the latex cleaning process. About 2mL of the synthesized emulsion raw material was weighed, proper amount of inhibitor-ethanol solution was added and then dried in a conventional oven at 90-100ºC to evaporate any unreacted monomers and water. The remaining solid was weighed and the degree of monomer conversion was determined. This process was repeated three times and a mean value of the degree of conversion was determined. Latexes were purified using a dialysis membrane to remove excess amount of surfactant and other water-soluble ionic materials. A regenerated cellulose dialysis membrane (MWCO 14000) was cleaned to remove soluble residual materials and was rinsed thoroughly with distilled water. A weighted amount of latex was placed inside the membrane and keep in a container with distilled water. Water was replaced every 12 h until the conductivity of the external water reached a constant value. The average diameter of latex particle was determined by a ZetaPALS Particle Sizing Instrument, at 25 ± 0.1 °C, every sample was measured 6 times and the average value was recorded as the average particle diameter. Measurements were made with solutions obtained by dispersing two drops of latex into distilled water. After intensive mixing, 2 ml aliquot was poured into the test cell, which was further sealed with a plastic stopper. NMR spectroscopy is a powerful technique used to provide detailed information on the molecular dynamics structure of molecules, can be used to investigate the filler-elastomer interface, crosslink density and the heterogeneity and structure of filled polymer networks [10]. In this paper crosslink density will be investigate using NMR spectroscopy with a AV 400, Bruker (USA), with dilution of polymer sample using chloroform-D as solvent. Titrimetry is widely used for determinations of acidic and basic functions such as carboxylic acid groups [11], epoxy groups [12-14], amine groups and other nitrogen-containing functions, and unsaturated groups [15]. TEM was used to verify the presence of chloro-functionalized polystyrene covering layer on SiO_2 particles. For TEM sample preparation, a drop of dilute filler suspension sample was placed on a carbon coated copper grid, left overnight in the dark, and dried. TEM image was obtained using H-800 TEM microscope (Hitachi – Japan), with an operating voltage of 200kV. SEM was employed to investigate surface morphology. First the sample surface was coated with gold and then exposed to the jet of electrons for imaging. SEM measurement was carried out with a Hitachi microscope (model: Hitachi S - 4700).

5. RESULTS AND DISCUSSION

The main objective of this paper was to investigate the preparation approach and product characterization of chloro-functionalized polystyrene reactive filler particles.

Increasement the number of functional groups on the particle surface is not only expected to affect crosslinking performance of the reactive filler, but also cause change in the stability of the dispersion during synthesis stage via emulsion approach and the latex property [15-16]. The procedure described above was carried out using emulsion polymerization. Various parameters effected the results such as chloro-functionalized polystyrene particles mass ratios, stirrer speed and different surfactant dosage, were investigated. Almost complete monomer conversion was obtained. Latex films were obtained by drying latex at drying oven at 60°C. The electrophoretic mobility of silicon dioxide was measured with different pH values using the ZetaPALS Particle Sizing Instrument. Using cationic initiator (AIBA) as driving force for the formation of SiO_2 / PSt (organic-inorganic composite).

5.1. Effect of Stirrer Speed

Stirrer speed has an important role in dispersing aqueous droplets containing water-soluble monomer in continuous oil phase where the formed emulsion is not thermodynamically stable [18, 19]. The effect of stirrer speed on conversion, average particle size of final emulsion was investigated in three different stirrer speeds, i.e. 330, 350, 370, 445 and 465 rpm. Were applied during the synthesis of nano-particles, whereas the other polymerization conditions were kept constant. By increasing the stirrer speed to 465 rpm, it is clear that size of monomer droplets and polymer particles decrease by increasing the stirrer speed. Therefore, the average size of the nano-particles decreased as the stirring rate increased from 330 to 465 rpm. Which indicate that stirring rate for sure effecting particle size, as illustrated in Table 1.

Table.1. Effect of stirring rate on the emulsion polymerization of reactive filler

Reactive filler	Mass ratio	Stirring speed (rpm)	Solid content designed (%)	Particle size（nm）
SiO_2-St- CMS	1 : 0.14 : 0.3	330	1.2	114.7 ± 2.2
SiO_2-St- CMS	1 : 0.14 : 0.3	350	1.2	99.5 ± 11.8
SiO_2-St- CMS	1 : 0.14 : 0.3	370	1.2	91.5 ± 30.8
SiO_2-St- CMS	1 : 0.14 : 0.3	445	1.2	90.9 ± 13.8
SiO_2-St- CMS	1 : 0.14 : 0.3	465	1.2	45.6 ± 3.7

Note: The particle size was measured by ZetaPALS Particle Sizing Instrument. The error was calculated as the standard deviation. Ingredients for the polymerization of all samples were equal.

It was attributed to the increased coalescence of polymer particles due to the higher stirrer speed. A probable reason is that high stirrer rate leads to desorption of the stabilizer molecule from the particle surface and the particles become so unstable that coagulation occurs [20]. There are some reports in the literature [21, 22] which
consider polymer particles with diameters as high as 250 nm as polymer nanoparticle because particle size distribution is in the range of 50-400 nm. Therefore, although average particle diameter data in the present work have been reported at rang of about 45.6 – 114.7 nm.

5.2. Effect of Surfactant Concentration

Emulsion polymerization of reactive filler was performed at various concentrations of surfactant. Increasing ionic surfactant amount used led to decrease in particle size as illustrated in Table 2.

Table.2. Effect of ionic surfactant dosage on final particle size of PSt-CMS filler particles

Reactive filler	Ionic surfactant SDS (%)	Solid content designed (%)	Particle size（nm）
St-CMS	3	14	101.4 ± 2.1
	5	14	78.1 ± 1.2
	7	14	53.6 ± 1.9

Note: The amount of ionic surfactant SDS was based on the total monomer mass. The particle size was measured by ZetaPALS Particle Sizing Instrument. The error was calculated as the standard deviation.

5.3. FTIR Spectroscopic Analysis

Functional group analysis of the pure St and functionalized polystyrene was carried out using Fourier transform infrared spectra of the polymer were recorded with a Nicolet model 6700 spectrometer in the range of 4000- 400 cm^{-1}. Small amounts of potassium bromide (KBr) and polymer samples were mixed. The mixture was placed in a mini press and was applied pressure to squeeze the KBr and polymer mixture into a thin, semi-transparent disk. The disks was then placed into FTIR instrument and infrared wave was passed through the disk to record the IR spectrum of the sample. Subtraction function in FTIR spectrum software was used for final results. FTIR spectra of the specimens were recorded to check copolymerization reaction between St and CMS. Figure 4 shows the characteristic band of the FTIR spectra for PSt and PSt/CMS composites absorbents, respectively. There are number of characteristic peaks for PS latex particles [23]. Aromatic C-H stretching vibration is shown at 3000 cm^{-1} and 3100 cm^{-1}, and aliphatic C-H asymmetrical and symmetrical stretching shown at 2900 cm-1and 2874 cm^{-1}, respectively. The peak at 699.80 cm^{-1} is the characteristic peak of polystyrene, the band due to CH bending vibrations of the aromatic ring at (700 cm^{-1} in the literature [24]). The series of peaks (1454.7, 1493.6 and1599.1cm^{-1}) in the region extending from 1400 to 1600 $cm^{-1}$are likely belongs to polystyrene [24]. There are number of characteristic peaks for chloromethylstyrene groups, the peaks at 1270.9 cm^{-1}(1270 cm^{-1} in the literature [25]), 1446.4 cm^{-1} (1447 cm^{-1} in the literature [26,27]) corresponds to (R)-CH_2-Cl stretching and 674.0 cm^{-1} (671 cm^{-1} in the literature [28]) attributed to halogen bonds in the chloromethyl groups which upon copolymerize with activated chains of polystyrene.

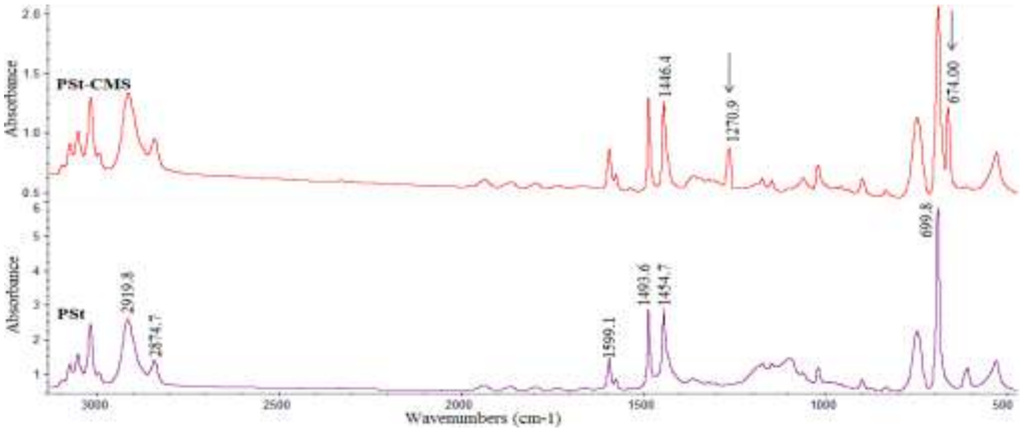

Figure 4. IR spectra of pure polystyrene and chloro-functionalized polystyrene

FTIR spectra of the specimens were recorded to check the organic–inorganic composite filler prepared from silicon dioxide, St and CMS. Figure 5 shows the characteristic band of the FTIR spectra for SiO_2 and PSt/CMS composites adsorbents, respectively, using subtraction function in FTIR spectrum software, such as SiO_2- PSt- CMS minus SiO_2- PSt. In FTIR spectrum of SiO_2, the peak at 1094.52 cm^{-1}can be assigned to Si–O–Si (1130–1000 cm^{-1} in the literature [27]). The additional bands in the spectrum of PSt/CMS particle, The band due to CH bending vibrations of the aromatic ring at (700 cm^{-1} in the literature [27]), so the peak at 699.80 cm^{-1} is the characteristic peak of polystyrene. The IR spectrum of CMS particle, the peaks at 1271.50 cm^{-1}(1270 cm^{-1} in the literature [28]), 1446.40 cm^{-1} (1447 cm^{-1} in the literature [29]) corresponds to (R)-CH_2-Cl stretching and 675.7 cm^{-1} (671 cm^{-1} in the literature [30]) attributed to halogen bonds in the chloromethyl groups.

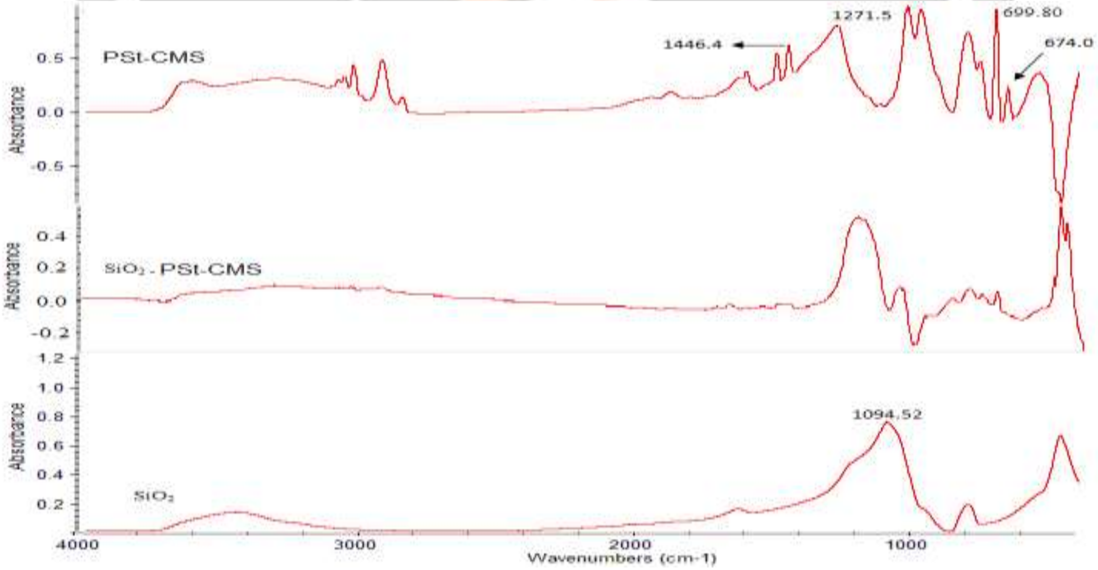

Figure 5. IR spectra of SiO_2 nanoparticles coated with chloro-functionalized polystyrene using subtraction function

5.4. Functional Group Density

Functional groups density incorporated on surface determined by both calculation method using equation 1 and NMR spectra Table 3. It is clear that increasing of reactive groups (CMS) mass ratio according to polystyrene (PSt) during polymerization, will increase functional groups density incorporated in particle sphere of reactive filler. It is considered that the reactive groups may present inside and on the surface of particle sphere of reactive filler.

$$N = \frac{n1}{[\frac{4}{3}\pi \times \left(\frac{d}{2}\right)^3 \times n2]} \qquad (1)$$

- N = average functional group number (m^{-3})
- n_1 = mole number of functional monomeric unit (CMS) in the particle (mol).
- n_2 = mole number of styrene unit in the particle (mol)
- d = average diameter of the particle (nm)

Table.3. Functional groups number

Monomer	Monomer mass ratio	Monomer conversion (%)	Particle Size (nm)	Functional group density (m^{-3})	Functional group per particle
CMS - St	0.02 : 0.98	98	96.4 ± 1.6	0.270×10^{20}	3.24×10^{4}
	0.04 : 0.96	98	95.0 ± 1.1	0.568×10^{20}	5.29×10^{4}
	0.06 : 0.94	98	96.5 ± 2.1	0.814×10^{20}	5.32×10^{4}
	0.08 : 0.92	97	97.3 ± 1.4	1.061×10^{20}	1.30×10^{5}
	0.10 : 0.90	98	101.2 ± 1.0	1.178×10^{20}	1.90×10^{5}

By using NMR method it was possible to confirm an apparent of the peak of chlorine groups which incorporated on the surface of polystyrene (reactive filler). The area under a peak in an NMR spectrum is proportional to the number of nuclei in a given chemical environment in a molecule. The intensity of an NMR peak gives information about the relative number of a given type of nucleus in a molecule. The peak around 4.5ppm confirms the presence of -CH_2-Cl moieties in the functionalized PSt particle Figure 6.

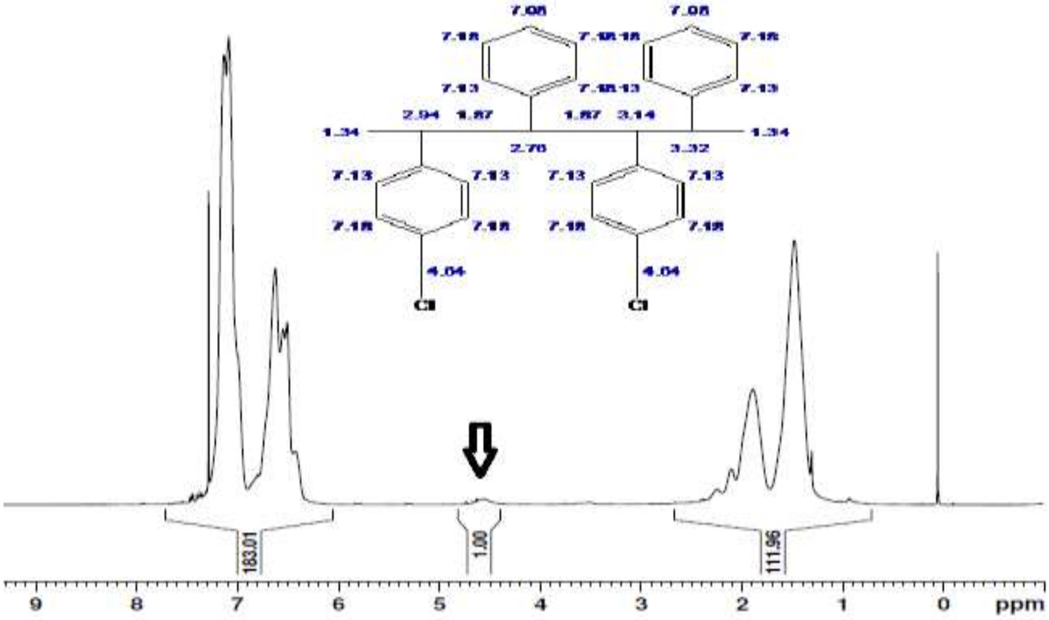

Figure 6 ^{1}HNMR for chloro-functionalized polystyrene

5.5. Morphology Observation

Using TEM was to provide a clear indication of morphology of the nanoparticles. A desired morphology of the particles has been achieved. TEM was used to verify the presence of the core and shell. TEM images indicated polystyrene successfully coated onto the surface of silicon dioxide particles, forming typical core/ shell morphology, as demonstrated in Fig 7. The dark core consists of primary SiO_2 particles and PSt located in its interstices, the surrounding light layer is PSt. These results can be compared with images of pure polystyrene (PSt) and pure SiO_2 as illustrated in Fig 8.

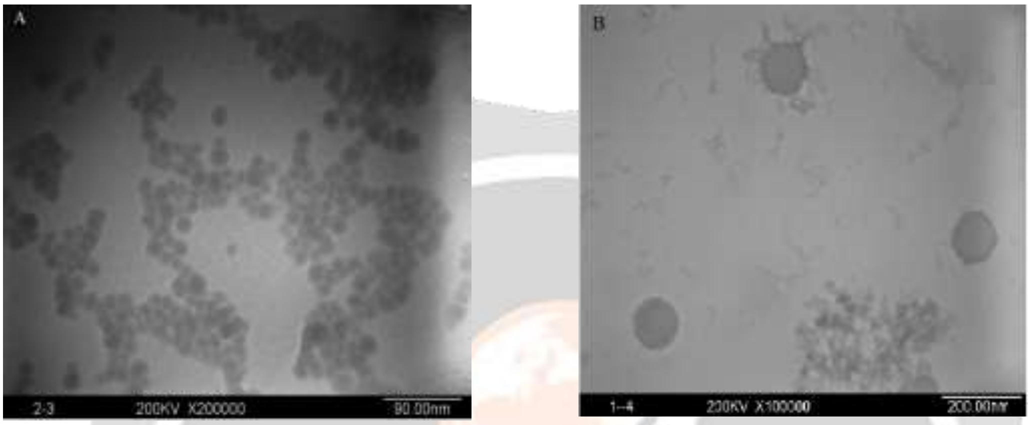

Figure.7. TEM images of (A) functionalized polystyrene coated onto the surface of SiO_2 nano-particles, (B) functionalized polystyrene coated onto the surface of SiO_2 nano-particles

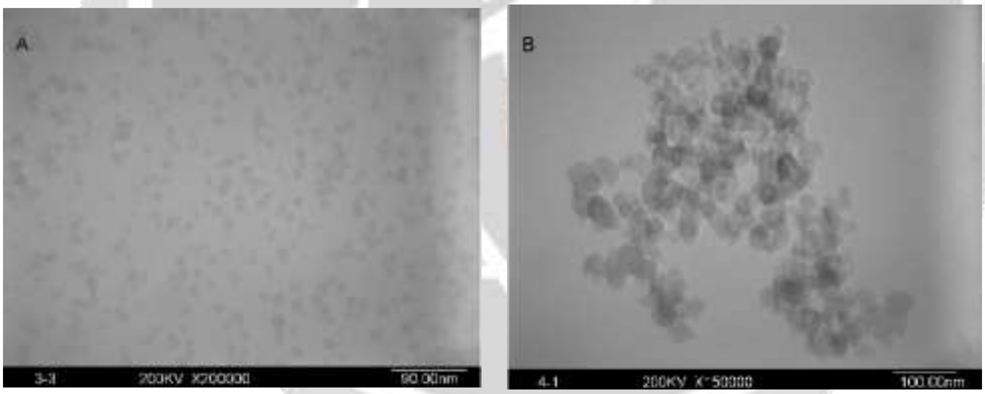

Figure.8.TEM images of (A) pure PSt nano-particles (B) pure SiO_2 nano-particles

6. CONCLUSIONS

Nano-scale reactive filler with high functionality content of chloro-reactive groups in both kinds of filler, spherical polystyrene with chlorine groups on surface and chloro-functionalized SiO_2-PSt organic-inorganic composite particles, were synthesized by emulsion polymerization. The stirrer speed (or shear rate) and the dosage of surfactant had clear effect on the size of filler particle obtained. As the increase of stirring rate and increase of surfactant dosage the particle size of filler microspheres decreased. Positively charged initiator (AIBA) was used to prepare organic-inorganic composite filler, which allowed deposition of St-CMS copolymer on negatively charged surface of SiO_2 particles. FTIR spectra of the specimens were recorded to check organic-inorganic composite. The peaks of SiO_2, PSt and chloromethylstyrene were quite clear. The results from particle size analysis and TEM observation showed that the composite particles were regularly spherical core/shell morphology.

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