



Synthesis of Silica/Polystyrene Nanocomposite Particles by Miniemulsion Polymerization

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Abstract

Miniemulsion polymerization is one of heterogeneous polymerization method that can be effectively used to synthesis of various novel organic-inorganic nanocomposite particles. This method can provide opportunity of good incorporation between the polymer and inorganic phases in the formed submicrometer-sized particles. In this article, we report preparation polystyrene/silica nanocomposite particles via miniemulsion polymerization of styrene (St). Synthesis of the nanocomposite particles were performed using γ -methacryloxypropyltrimethoxysilane (MPS) which perform compatibility of silica and the polymer phase by covalent interactions. Morphology, particle size, spectroscopic characteristics and thermal properties of resulted nanocomposite particles were studied. TEM study showed a raspberry like morphology for the nanocomposite particles. FT-IR spectroscopy confirmed the presence of polystyrene and silica with MPS compatibilizer in the structure of the nanocomposite. Thermogravimetric analysis and Differential scanning calorimetry studies showed that the incorporation of silica in polymer matrix results variation in thermal stability and glass transition temperature of nanocomposite particles relative to that of the polymer without silica in it.

Keywords: Polystyrene nanocomposite particles, Silica, Miniemulsion polymerization.

Introduction

Preparation of polymer/inorganic nanocomposites in a dispersion system can present a new class of composites with different properties from the individual inorganic or polymeric particles. Nanocomposite synthesis can be done at *in situ* heterophase polymerization including emulsion, miniemulsion, suspension and dispersion polymerization [1-5]. Among the techniques, miniemulsion polymerization method is very suitable for preparation of polymer/inorganic nanocomposites [6,7]. However the different surface properties of inorganic particles and polymer are main issue to appropriate incorporation of inorganic particle and polymers. For the success in formation of the nanocomposite particles, it is necessary to use some interfacial promoters to create specific interaction and increase interfacial adhesion between the hydrophilic inorganic and hydrophobic polymer phases. Utilization of appropriate functional agents such as comonomers, initiators or surfactants are common approaches to increase compatibility of the inorganic phase in polymer matrices [8, 9]. The reagents attach to the inorganic surfaces via covalent, coordination or hydrogen bonds or ionic interactions to promote compatibility between inorganic and organic phases. The reagents may be bear different reactive groups which introduce in miniemulsion polymerization reactions. For example, surface charge attraction between

cationic groups of the hydrophilic monomer and acidic surface character of inorganic particles is a driving force for nanocomposite synthesis. 4-vinylpyridine [10, 11], 1-vinylimidazole [12], 2-(dimethylamino)ethyl methacrylate [13] or 2-(methacryloyl)ethyltrimethylammonium chloride [14] can improve performance of polymer nanocomposite formation via the electrostatic interactions. γ -methacryloxypropyltrimethoxysilane (MPS) is another common coupling agent which promote compatibility between organic and inorganic phases via covalent interactions between them [15-19]. Such effects can be appropriately used in preparation of silica/polymer nanocomposite particles during polymer synthesis. The nanocomposites latex may be used as exterior coatings which have improved physical and mechanical properties.

In this study, we reported synthesis of polystyrene/silica nanocomposite particles by miniemulsion polymerization. In the synthesis process we made use of MPS as adhesion promoter between the polystyrene and silica phases. MPS can create covalent bonds between the polymer and silanol groups of silica. Some thermal properties and IR characteristics of the resulted nanocomposite particles were investigated.

Experimental

Styrene (St, Merck, $\geq 99\%$) was purified by distillation under reduced pressure before use.

γ -methacryloxypropyltrimethoxysilane (MPS, Aldrich, 98%), azobisisobutyronitrile (AIBN, Aldrich, 98%), tetraethyl orthosilicate (TEOS, Merck, 99%), the nonionic polyoxyethylene octylphenol surfactant with average number of ethylene oxide units of 40 (TX-405, Aldrich, 70% solution in water) were used as received.

The polystyrene/silica nanocomposite particles were prepared by free radical miniemulsion polymerization of with MPS as comonomers initiated by AIBN. Silica phase was produced by hydrolysis-condensation of TEOS under basic condition [20]. TEOS is one of the most common silica precursors which is used in preparation of silica nanoparticles in laboratory scale. The mini-emulsification of the reactants in water was performed by sonication for 120 s at 90% amplitude with a Branson W450 sonifier. The miniemulsion reactions were performed at 70 °C under nitrogen atmosphere for 24 hr.

The morphology of the particles was examined by transmission electron microscopy (TEM) using a Carl Zeiss CEM 902 with an accelerating voltage of 80 kV. Average particle size measurements were performed using a Malvern Nano-ZS instrument. The infrared spectra were recorded using a Bruker EQUINOX FTIR spectrometer. The thermal degradation behavior and the polymer content of the samples were conducted with a TA Q50 thermogravimetric analyzer (TA Instruments). The dried purified samples were heated in a

flow of argon, from room temperature to 700 °C at a scan rate of 20 °C/min. Differential scanning calorimetry analysis was carried out with a TA Q100 (TA Instruments), at a heating rate of 10 °C/min between 0 °C and 180 °C under argon atmosphere.

Results and discussion

Miniemulsion is a typical dispersion system that reactant are distributed in water as droplets with size range 50-500 nm [21]. The miniemulsion droplets can be considered as a nanoreactor which can be utilized for in situ preparation of various nanocomposite particles such as polystyrene/silica nanocomposite with sufficient combination between polystyrene and silica phases in this system. The polymerization was performed with 0.43 mol/L Styrene miniemulsified in water by TX-405. TX-405 is a common non-ionic surfactant which used in (mini)emulsion polymerizations. The surfactant not only stabilizes miniemulsion system but also has minimum effect in the nanocomposite formation process, which is desirable in our experiments for showing importance of covalent interaction between polystyrene and silica in the nanocomposite formation. As compatibility of forming hydrophobic polystyrene with the hydrophilic silica phase is low we applied 0.075mol/L of MPS to perform a suitable covalent interaction between silica and polystyrene. In this condition it was shown the polymerization

was performed in a stable state whereas in the lack of MPS the system was unstable and leads to precipitate. Thus MPS had important role in formation of the nanocomposite particles. The size of the resulted polystyrene/silica nanocomposite particles was 219 nm with PDI 0.12 measured by DLS.

TEM study of the nanocomposite particles showed a raspberry like structure in which the silica particles are disposed at nanocomposite shell (Figure 1).

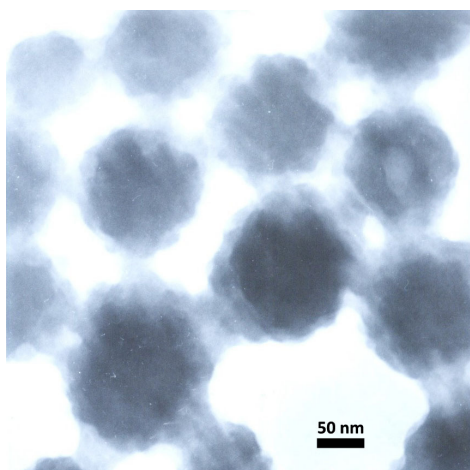


Figure 1. TEM image of the polystyrene/silica nanocomposite particles.

Figure 2 shows FTIR spectra of the polystyrene homopolymer (spectrum a) prepared by miniemulsion polymerization and polystyrene/silica nanocomposite product (spectrum b). In the spectra of figure 2, The bands observed at $>3000\text{ cm}^{-1}$ and 1601 cm^{-1} are respectively due to C-H and C-C vibration modes of phenyl ring of the styrenic units which are common in spectrum (a) and (b). In spectrum (b) strong peak around 1083 cm^{-1} caused by

stretching vibration modes of Si-O-Si bands of silica, band at 1723 cm^{-1} corresponding to C=O stretching vibration MPS segments. The spectrum confirms the presence nanocomposite composed by silica and polystyrene which are compatibilized by MPS.

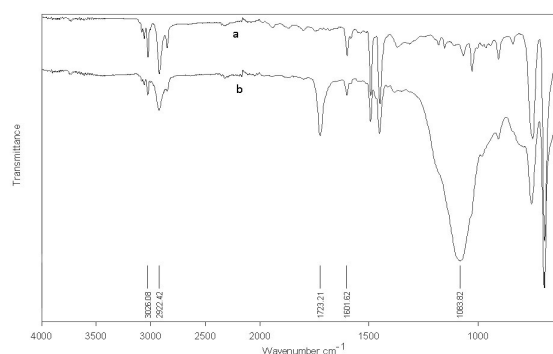


Figure 2. FTIR spectra of a) polystyrene and b) polystyrene/silica nanocomposite.

Thermal degradation of the silica/polystyrene nanocomposite was analyzed by thermogravimetric analysis (TGA) method. Figure 3 show thermal degradation as a function of temperature for silica/polystyrene nanocomposite. Thermogram of polystyrene homopolymer was also shown in Figure 3 for comparison. Thermogram of polystyrene shows the onset and end point of decomposition of polystyrene at $335\text{ }^{\circ}\text{C}$ and $463\text{ }^{\circ}\text{C}$ respectively. The nanocomposite starts to predominant decomposition at about $290\text{ }^{\circ}\text{C}$ which $45\text{ }^{\circ}\text{C}$ lower than that polystyrene. The lower decomposition temperature hints effect of silica on stimulation of degradation of polystyrene. But it is shown silica/polystyrene nanocomposite ends up thermal

degradation at about 550 °C which even higher (87 °C) than corresponding polystyrene decomposition endpoint. The enhancement of thermal stability at the end of degradation can be regarded as an evidence of interaction between the organic polymer and silica nanoparticles. At above 550 °C the thermogram tends to constant weight related to silica as residue of the nanocomposite. The silica content of the nanocomposite calculated with TGA was 27 wt.%.

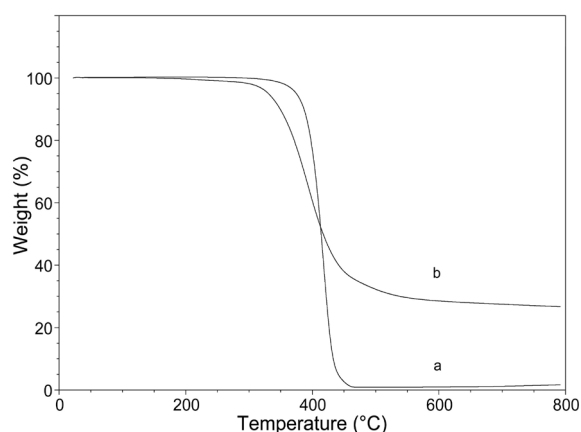


Figure 3. Thermogravimetric degradation curves for a) polystyrene, b) polystyrene/silica nanocomposite.

Effect of incorporation of silica on glass transition temperature (T_g) of polystyrene matrix of the nanocomposite product was studied by Differential Scanning Calorimetry (DSC). DSC thermograms of the polystyrene product and the corresponding silica nanocomposite are shown in Figure 4. In polystyrene thermogram a discernible glass transition is shown at 93.7 °C whereas no transition is detectable in thermogram of the silica/polymer nanocomposite. It can be

considered as a direct consequence of lower mobility of polymer chains due to strong covalent interactions which created via MPS between polystyrene and silica phases [22]. The organic-inorganic interactions minimize segmental motions of polystyrene chains so effective to cannot be detected by DSC analysis.

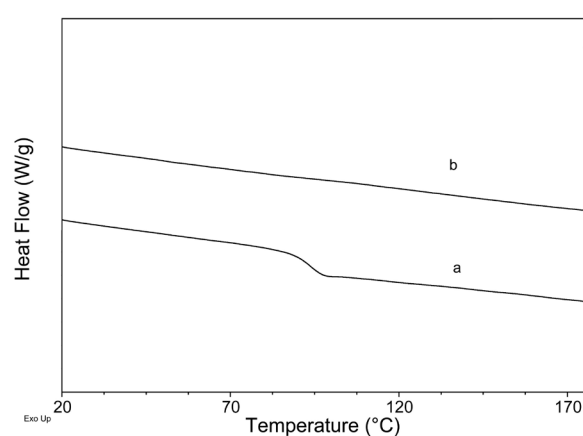


Figure 4. DSC curves for the composite products a) polystyrene, b) polystyrene/silica nanocomposite.

Conclusion

In this work, raspberry like silica/polystyrene nanocomposite particles were successfully prepared via miniemulsion polymerization. In this system MPS was used as compatibilizer to improve adhesion between silica and polystyrene phases. Covalent interaction of MPS with the surface of silica phases ensures the nanocomposite formation. The presence of silica and polystyrene along with MPS in the nanocomposite particles was shown by FTIR study. Thermogravimetric analysis showed in spite of influence of silica on acceleration

of initial decomposition of polystyrene, the nanocomposite was more stable at final decomposition process. As indicated in DSC analysis, presence of covalent interactions between silica and polystyrene phases caused major reduction in segmental motions in polystyrene chains. The results of all of the analyses are evidences of formation the inorganic/polymer nanocomposite with good compatibility of the phases in it.

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References

- [1] C. W. Chen, T. Serizawa, M. Akashi, *Chem. Mater.*, 11, 1381 (1999).
- [2] D. B. Mitzi, *Chem. Mater.*, 13, 3283 (2001).
- [3] T. Vossmeier, B. Guse, I. Besnard, R. E. Bauer, K. Mullen, A. Yasuda, *Adv. Mater.*, 14, 238 (2002).
- [4] E. Duguet, M. Abboud, F. Morvan, P. Maheu, M. Fontanille, *Macromol. Symp.*, 151, 365 (2000).
- [5] E. Bourgeat-Lami, J. Lang *J. Colloid Interface Sci.*, 197, 293 (1998).
- [6] E. Bourgeat-Lami, *J. Nanosci. Nanotech.*, 2, 1 (2002).
- [7] M. Antonietti, K. Landfester, *Prog. Polym. Sci.*, 27, 689 (2002).
- [8] D. G. Hawthorne, J. H. Hodgkin, B. C. Loft, D. H. Solomon, *J. Macromol. Sci. Chem.*, A8, 649 (1974).
- [9] M. E. J. Dekkers, D. Heikens, *J. Appl. Polym. Sci.*, 28, 3809 (1983).
- [10] F. Tiarks, K. Landfester, M. Antonietti, *Langmuir*, 17, 5775 (2001).
- [11] X. G. Qiao, M. Chen, J. Zhou, L. M. Wu, *J. Polym. Sci. A Polym. Chem.*, 45, 1028 (2007).
- [12] Y. Zhang, H. Chen, Q. Zou, *Colloid Polym. Sci.*, 287, 1221 (2009).
- [13] M. Barari, N. Sharifi-Sanjani, *J. Appl. Polym. Sci.*, 110, 929 (2008).
- [14] Y. Zhang, H. Chen, X. Shu, Q. Zou, M. Chen, *Colloids Surf., A*, 350, 26 (2009).
- [15] S. W. Zhang, S. X. Zhou, Y. M. Weng, L. M. Wu, *Langmuir*, 21, 2124 (2005).
- [16] J. Zhou, M. Chen, X. G. Qiao, L. M. Wu, *Langmuir*, 22, 10175 (2006).
- [17] X. G. Qiao, M. Chen, J. Zhou, and L.M. Wu, *J. Polym. Sci. A Polym. Chem.*, 45, 1028 (2007).
- [18] O. Töpfer, G. Schmidt-Naake, *Macromol. Symp.*, 248, 239 (2007).
- [19] A. Costoyas, J. Ramos, J. Forcada, *J. Polym. Sci. A Polym. Chem.*, 47, 935 (2009).
- [20] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.*, 26, 62 (1968).
- [21] U. El-Jaby, M. Cunningham, T.F.L. McKenna, *Ind. Eng. Chem. Res.*, 48, 10147 (2009).
- [22] C. E. Porter, F. D. Blum, *Macromolecules*, 33, 7016 (2000).