

Synthesis of Polystyrene Grafting Filler Nanoparticles: Effect of Grafting on Mechanical Reinforcement

M. Khelifa, A. Youssef, A. F. Zaed, A. Kraft, V. Arrighi

Abstract—A series of polystyrene (PS) nanoparticles were prepared by grafting polystyrene from both aggregated silica and colloidal dispersed silica nanoparticles using atom-transfer radical polymerisation (ATRP). Cross-linking and macroscopic gelation were minimised by using a miniemulsion system. The thermal and mechanical behaviour of the nanocomposites have been examined by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA).

Keywords—ATRP, nanocomposites, polystyrene, reinforcement.

I. INTRODUCTION

THE addition of filler material into a polymer can affect the mechanical properties of the polymer composite, including its toughness, durability and strength [1]. While some filler materials are quite cheap (e.g. carbon black, talc and silica), others such as glass fibres and carbon nanotubes are considerably more expensive [2]. Silica nanoparticles are of particular interest since they are commercially available both in aggregated and non-aggregated form, as well as in a range of sizes, with diameters as small as 7–20 nm and their high surface-to-volume ratio promises excellent compatibility with many polymer matrices [3]. Polymer filler composites are often prepared by solution dispersion due to its simplicity which involves dispersing the particles in a polymer solution followed by evaporation the solvent [3], [4]. From a chemical point of view, silica particles are relatively easy to functionalise and modify. In particular, a suitable surface treatment makes silica hydrophilic or hydrophobic, and thus helps to improve the filler's compatibility with a surrounding polymer matrix. Several recent papers have demonstrated already that polymer chains can be grafted onto silica and alumina particles by controlled radical polymerisation [5]–[7].

The most prominent method is atom-transfer radical polymerisation (ATRP), which has the added advantage that the functionalisation of silica particles with a suitable initiator is straight forward and allows polymer chains to be grown from the silica surface in a narrow size distribution. In contrast, nitroxide-mediated polymerisation (NMP) and reversible addition fragmentation chain transfer (RAFT) polymerisation seem to be more restricted with regard to the

choice of monomer and require a more elaborate synthesis for the surface initiating group [5], [8]. In this paper, we report how the addition of a suitably modified silica nanoparticles improves the mechanical and thermal properties of polystyrene–silica nanoparticles.

Despite their potential wide-ranging engineering applications, very little is known about the effect of surface-grafted filler particles on the mechanical and thermal properties of the resulting nanocomposites. PS has been extensively used as a hard segment in copolymers for nanocomposite applications due to its low cost compared to other polymers such as polycarbonate and PMMA [1]. Although few studies have been carried out on the dynamic mechanical properties of PS-silica nanoparticles, there has been no comprehensive study about the effect of surface-grafted silica particles on mechanical properties of the resulting nanocomposites. Most mechanical studies have concentrated on either unmodified nanosilica or commercially available surface-modified particles' incorporation in polystyrene [9]–[13]. Furthermore, most other groups have either chosen aggregated or non-aggregated silica nanoparticles, but never compared the effect of surface-grafted filler particles on the thermal and mechanical properties of nanocomposites made using both types of silica [14]. Since the type of silica particles is known to significantly influence the properties of the polymer composites is instructive to carry out comparative studies [15]. Reactive silica particles have already been converted into PS composites. These studies were carried out by dispersing non-aggregating spherical silica nanoparticles, which were either untreated or surface-modified, in styrene monomer, followed by polymerisation using a free radical initiator. Although chemical bonds between organic and inorganic phase are likely to exist in such cases, the free radical polymerisation process also produces free polymer chains, unattached to the silica surface [10], [11], [16], [17]. This is therefore different from the grafting process described here. To be able to compare the properties of PS-grafted particles to those of more conventional PS/nanosilica composites, we prepared also a series of samples by dispersing silica nanoparticles in a tetrahydrofuran (THF) solution of PS and investigated their mechanical behavior using dynamic mechanical thermal analysis (DMTA).

II. EXPERIMENTAL

Polystyrene (M_n 110,000 g/mol, T_g 98–100°C) was supplied by Dow Chemical Company and styrene, ascorbic acid, N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA), and Brij 98 were purchased from Aldrich; Copper (II) chloride,

M. Khelifa is with the Department of Chemistry, University of Sebha, Libya (corresponding author to provide phone: 00218 92 5237021; e-mail: Mask1@hw.ac.uk).

A. Youssef is with the Department of Chemistry, University of Sebha, Libya.

A. Kraft is with the Institute of Chemistry, Heriot Watt University, UK

V. Arrighi is with the Institute of Chemistry, Heriot Watt University, UK (e-mail: V. Arrighi@hw.ac.uk).

tetrabutylammonium fluoride (TBAF), and triethylamine from Lancaster; 3-aminopropyltriethoxysilane and hexadecane from Fluka; and ethylenediaminetetraacetic acid disodium salt (EDTA) from Acros. Hydrophilic Cab-o-sil H5 silica particles with a specific surface area of $300 \pm 30 \text{ m}^2/\text{g}$ and a diameter of 7 were obtained from Cabot and a 30% solution MEK-ST Colloidal silica, having a particle size between 10-15nm from Nissan Chemical. Aerosil 300 was a gift from Degussa-Hüls (Hanau, Germany).

A. Preparation of Polystyrene-Silica Composites by Dispersion

A 5% solution of PS in THF along with the required amounts of dried filler particles (Aerosil 300, MEK-ST) were added to a beaker. The beaker was sealed with Nesco film to prevent evaporation of the solvent and stirred for 48 hours. The solvent was then allowed to evaporate at room temperature. Samples were dried in an oven at 160°C for 24 hours to remove all solvent residues.

B. Preparation of 2,2,2-Trichloroethyl Carbamate Initiator

A mixture of 3-aminopropyltriethoxysilane (13.6 mL, 12.9 g, 58.4 mmol), 2,2,2-trichloroethyl chloroformate (7.9 mL, 12 g, 58 mmol), and triethylamine (10.0 mL, 7.26 g, 71.7 mmol) in toluene (100 mL) was stirred at 40°C for 4 hours. The reaction mixture was filtered to remove triethylammonium chloride. The filtrate was concentrated in vacuum to give a yellow-brown oil (20.6 g, 89%). For analysis, the crude product was further purified by vacuum distillation (Kugelrohr, $205^\circ\text{C}/0.4 \text{ mbar}$) to yield product as a colourless liquid. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 0.64 (t, $J = 7.9 \text{ Hz}$, 2 H), 1.22 (t, $J = 7.1 \text{ Hz}$, 9 H), 1.67 (tt, $J = 7.9, 6.6 \text{ Hz}$, 2 H), 3.24 (q, $J = 6.6 \text{ Hz}$, 2 H), 3.82 (q, $J = 7.1 \text{ Hz}$, 6 H), 4.71 (s, 2 H), 5.38 (br. t, 1 H). $^{13}\text{C NMR}$ (50 MHz, CDCl_3): δ 7.52 (CH_2), 18.16 (CH_3), 22.88 (CH_2), 43.47 (CH_2), 58.35 (CH_2), 74.29 (CH_2), 95.62 (C), 154.47 (C=O). IR (KBr, cm^{-1}): ν 3338 (bs), 2974 (s), 1733 (s), 1538 (s), 958 (s). MS (CI, NH_3): m/z 417, 415, 413 (1, 3, 3%), 352, 350 (9, 10), 265 (27), 222 (100), 208 (25), 176 (33). Exact mass calcd. for $\text{C}_{12}\text{H}_{24}^{35}\text{Cl}_3\text{NO}_5\text{Si} + \text{NH}_4^+$ requires m/z 413.0828, found 413.0826 (CI, NH_3). Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{NO}_5\text{Si}$ (396.8): C, 36.33; H, 6.10; N, 3.53. Found: C, 35.88; H, 5.72; N, 3.53.

C. Synthesis of Trichloroethyl Carbamate Functionalised Silica Nanoparticles

Silica nanoparticles were dried at $110^\circ\text{C}/0.03 \text{ mbar}$ for 6 hours. A slurry of silica nanoparticles (5.1 g), trichloroethyl carbamate initiator (273 mg, 0.688 mmol), and toluene (90 mL) was heated to 110°C for 12 hours. The solid was centrifuged (4000 rpm, 20 min) and the supernatant decanted. Centrifugation-decantation was repeated 3 times with THF as the extracting solvent. The gel layer was transferred into a pre-weighed beaker and dried in an oven at 60°C overnight.

D. ATRP of Styrene from Trichloroethyl Carbamate Functionalised Silica Nanoparticles

Copper (II) chloride (5.1 mg, 38 μmol), PMDETA (6.5 mg, 8 μL , 38 μmol), inhibitor-free styrene (4.0 mL, 3.6 g, 34.8

mmol), and deionised water (3 mL) were continuously stirred in Schlenk flask at 50°C for 15 min. The solution became blue due to the presence of a copper (II) amine complex. The solution was then cooled in an ice bath. A solution of Brij (115mg) in deionised water (17 mL), hexadecane (0.23 mL) and trichloroethyl carbamate-initiator functionalised silica nanoparticles (0.61 g) were added to the Schlenk flask. The solution was then sonicated for 7 minutes. The homogenised miniemulsion was then deoxygenated with nitrogen for 30 minutes before being heated at 90°C in a poly (ethylene glycol) bath. An aqueous solution of ascorbic acid (8.0 mg, 46 μmol , dissolved in 0.8 mL of deionised water) was added to initiate the polymerisation. The polymerisation was stopped after 2 days. An aqueous solution of EDTA (15.5 mg, dissolved in 3 mL of deionised water) was then added in order to extract the copper complex. The solid was collected by suction filtration and washed with methanol (20 mL). After suspension of the solid in deionised water (50 mL), this procedure was repeated once, and the crude product further purified by Soxhelt extraction with THF (100 mL, 12 hours at 90°C). The residual was dried for 24 hours in an oven at 160°C . Yield 3.10 g.

DSC

Differential scanning calorimetry (DSC) analyses were performed with a Thermal Advantage DSC 2010 at a heating rate of $20^\circ\text{C min}^{-1}$ under a constant nitrogen flow. Glass transition temperatures were taken as the mid-point of the transition.

DMTA

A TA Instruments DMA 2980 dynamic mechanical analyser was used in the single cantilever mode at a frequency of 1 Hz and a heating rate of 2°C min^{-1} . Samples were prepared in a rectangular mould using a hot press at 200°C and applying a weight of 5 tons for 30 minutes.

III. RESULT AND DISCUSSION

A. DSC and DMTA Analysis of Dispersed PS/Silica Nanoparticles

The DSC results of the PS-Aerosil 300 composites are shown in Table I. DSC results indicated only small changes in the glass transition temperature (T_g) between neat polystyrene and PS-A300 composites: T_g values of composites containing 10wt%, 20wt%, or 30wt% of silica are very close. This result was found with PS-dispersed silica such as MEK-ST. wide variety of polymer-silica composites have shown interesting changes in the bulk T_g values [18]. Many researchers have studied the effect of the filler materials on T_g and have drawn different conclusions. Most of the researches reported an increase in the glass transition temperature as a function of filler content [19], [20] however, decreases or no effect on the glass transition of the polymer composites also have been found [21], [22]. Furthermore, the DSC measurements also reveal changes in heat capacity, ΔC_p . It should be mentioned that the ΔC_p value of PS decreases with increasing the amount of filler added. The decrease in ΔC_p could be attributed to the

formation of rigid amorphous fraction in the composites [23].

TABLE I
GLASS TRANSITION TEMPERATURE FOR VARIOUS COMPOSITES

Sample	T_g / °C
Pure PS	100.0
PS-A300 10 wt%	100.1
PS-A300 20 wt%	100.3
PS-A300 30 wt%	100.2

More significant differences were observed in the DMTA data. Fig. 1 shows an example of a series of storage modulus vs. temperature curves for PS-A300 composites. Whereas neat PS samples deformed already at a temperature of 135°C (roughly 35°C above the T_g of the polymer) and the DMTA run stopped at 155°C as a result of sample disintegration, the addition of only 10 wt% silica nanoparticles delayed sample deformation significantly and made it possible to extend the DMTA measurement to up 200°C. In addition, there is an increase in the modulus above the glass transition with increasing filler concentration.

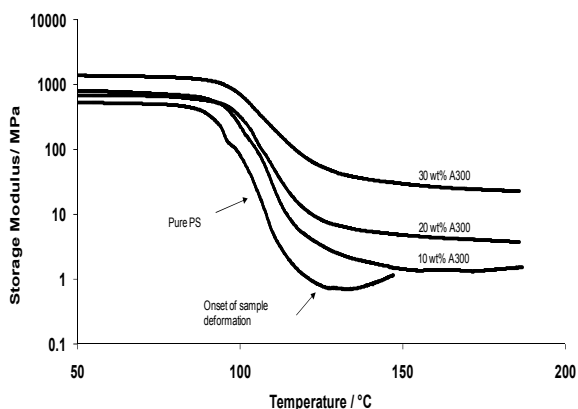


Fig. 1 Plot of storage modulus as a function of temperature for pure PS and various PS/Aerosil 300 nanocomposites

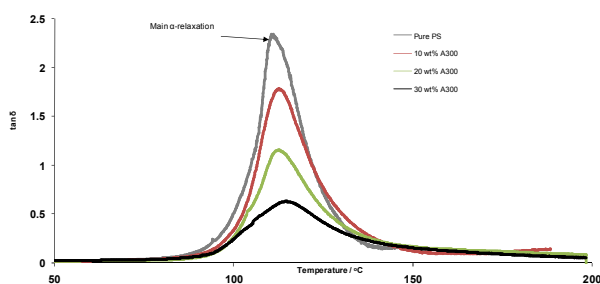


Fig. 2 Plot of $\tan \delta$ as a function of temperature for pure PS and various PS/Aerosil 300 nanocomposites

The $\tan \delta$ peak at the main α -relaxation, which is generally associated with the T_g , showed a decrease with increasing silica content as shown in Fig. 2. It should be mentioned that, no second $\tan \delta$ peak (second maximum) was observed at higher temperature. In many previous studies on filler polymer composites, the existence of a second relaxation peak, or β relaxation, in the $\tan \delta$ curves has been reported. This peak appears as a shoulder at a temperature above α relaxation

peak. For example, Tsagaropoulos and Eisenberg reported that there are two peaks in the $\tan \delta$ curve for PVAc-silica nanoparticles. The second peak was located at 100 °C above the main α relaxation peak (T_g). They attributed the second peak to the glass transition temperature of immobilised chains near the particles [20].

B. DSC and DMTA Analysis of Grafted Ps/Silica Nanoparticles

Fig. 3 shows the synthetic scheme used to graft PS from the surface of silica nanoparticles. ATRP initiator was conveniently prepared in one step from commercially available starting materials. A literature procedure for ATRP in miniemulsion, introduced by Matyjaszewski et al., was opted since this process was straightforward and had already been demonstrated to work successfully for grafting poly(butyl acrylate) from the surface of colloidal dispersed silica nanoparticles [6]. After the polymerisation had finished, care was taken to remove any unattached polymer through extensive Soxhlet extraction of the crude product. A small sample of the hybrid particles was treated with tetrabutylammonium fluoride to detach the polymer from the silica particles [22]. GPC measurements (THF, polystyrene standards) of a typical cleaved PS sample revealed an M_n of 83,000 g/mol and a polydispersity index of 1.8. The broadened polydispersity was probably due to our choice of a water-soluble chelating amine ligand (PMDETA), which reduced the concentration of the active copper complex in the organic monomer phase.

PS-silica composites with various molecular weights and silica content were studied by DSC. As illustrated in Fig. 4 the glass transition temperatures of the hybrid material are usually higher compared to neat PS, which indicated a strong interaction between PS and silica nanofiller when linked together by a covalent bond [24].

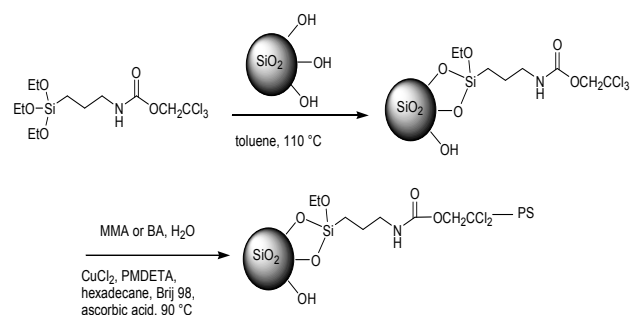


Fig 3 Synthetic scheme for the grafting of polystyrene from silica nanoparticles using ATRP in miniemulsion

The T_g increase observed for the grafted systems compared to pure PS seems to be dependent on the molecular weight of the grafted chains as well as nanosilica content and type. For example, for the grafted PS-MEK-ST with lowest M_n , G32-10Si, the T_g is close to that of neat PS. In this case, the expected decrease due to the low molecular weight is probably offset by the relatively high silica content, leading to a T_g close to that of pure PS. It is interesting to find that the grafted PS-

Cab-o-sil H5 composite (G26-10Si) has a higher T_g than the grafted PS-MEK-ST (G32-10Si) with similar silica content and closer molecular weight. This fact indicates that the glass transition of the composites is also strongly dependent on the nature of the silica (i.e. aggregated or non-aggregated). This could be due to the decrease in the segmental mobility of grafted chains with aggregation of nanoparticles [24]. Overall these observations indicate that the T_g values of the grafted PS samples increase with the silica content. The trend observed for the $\tan \delta$ maxima is consistent with the DSC results.

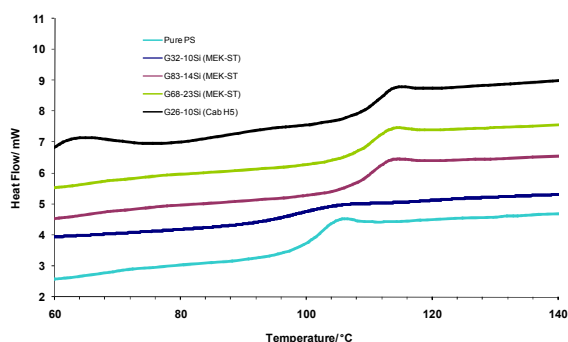


Fig. 4 DSC traces of pure PS and grafted PS-silica. G32-10Si (MEK-ST). "G32" refers to a number-average molecular weight of 32 kg mol⁻¹ for the grafted PS, "10Si" stands for a silica content of 10 wt%

Fig. 5 shows the change in storage modulus as a function of temperature for a pure polystyrene sample and for polystyrene grafted from silica nanoparticles. A substantial increase in the modulus was observed for all polystyrene-silica nanocomposites at temperatures above T_g . This reinforcement was more pronounced with larger amounts of colloiddally dispersed silica content and, even more so, when aggregated silica nanoparticles were used. The modulus vs. temperature plot for unfilled PS reveals an onset of deformation at about 130–140°C, which is no longer seen in the grafted polystyrene-silica nanocomposites. At silica contents >10 wt% DMTA tests could be extended to 200 °C, in some cases even up to a temperature of 250°C — more than 130°C above the T_g of PS. No second transition at ~65°C and well below T_g was evident from the modulus vs. temperature curves which had been noted by others and attributed to chain mobility in polymer-silica composite systems [25]. Grafting PS from aggregated Cab-o-sil H5 silica nanoparticles led to an even higher storage modulus than grafting PS from colloiddally dispersed silica (MEK-ST). Such a substantial increase of storage modulus can be attributed to the formation of a 3-dimensional network of silica nanoparticles (with Cab-o-sil H5), which is not possible when the polymer was grafted from the surface of colloiddally dispersed silica (MEK-ST). A similar trend was previously observed for PMMA-silica nanocomposites [26]. Aggregated silica nanoparticles possess an additional dimensional network that further strengthens the composites. However, TEM showed no evidence of aggregation for colloiddally dispersed silica nanoparticles (G83-14Si) as shown in Fig. 6. Whether or not the polymer itself is part of a 3-dimensional network (due to combination

of growing polymer chain radicals originating from different silica particles) cannot be ruled out and is subject to further investigation.

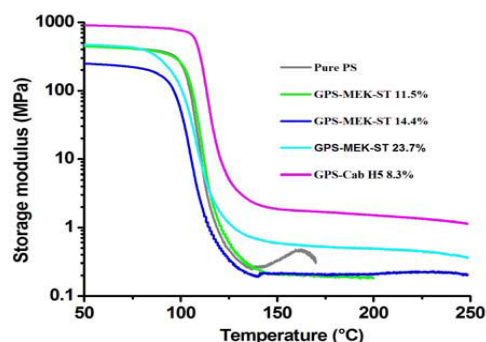


Fig. 5 Plot of storage modulus as a function of temperature for PS and grafted PS-silica nanocomposites for various types of silica nanoparticles (MEK-ST or Cab-o-sil H5) and percentage content

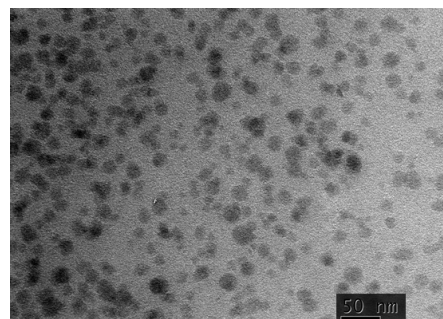


Fig. 6 TEM image of a grafted PS-silica composite

Fig. 7 displays plots of $\tan \delta$ as a function of temperature for various PS-silica composites. The main $\tan \delta$ peak is generally associated with the glass transition and found at a temperature roughly 8–10°C above the T_g determined by DSC. Only the T_g of the grafted aggregated silica (Cab-o-sil H5) was slightly higher by about 4°C. The size of the $\tan \delta$ peak decreases with increasing filler content, which suggests that the mobility of the polymer was reduced in the hybrid materials that make up the composites. At elevated temperature well above T_g , a high silica content lowered $\tan \delta$ to small values close to zero, indicating that the composites softened but remained elastic and were able to recover from small deformation.

This study suggests that the grafting of a polymer from the surface of silica nanoparticles improves not only the modulus but also the high temperature properties of the composite. The effect tends to be more pronounced when the silica nanoparticles are aggregated (e.g. Cab-o-sil H5), and less so when they are dispersed (MEK-ST). While the attachment of the polymer chains to the silica nanoparticle filler already makes the composite less susceptible to breaking at high temperature, the additional improvement is attributed to the presence of a 3-dimensional network of silica nanoparticles.

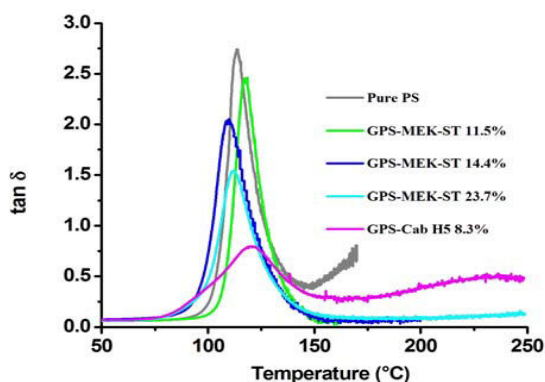


Fig. 7 Plot of $\tan \delta$ as a function of temperature for pure PS and grafted PS-silica nanocomposites for various types of silica nanoparticles and percentage content

IV. CONCLUSION

Using an ATRP in miniemulsion procedure, polystyrene was successfully grafted from both non-aggregated and aggregated silica nanoparticles that possessed a high tendency to aggregate. While the T_g of the polymer remained remarkably unaffected, the attachment of PS to silica nanoparticles provided a hybrid material with virtually no high-temperature damping and an extended, reinforced, rubbery plateau at elevated temperature that is comparable to that of crosslinked polymers. Further work is currently in progress.

ACKNOWLEDGMENT

“Dr. Khelifa thanks the University of Sebha for financial support, as well as Cabot GmbH (Hanau, Germany) and Nissan Chemical for a gift of silica nanoparticles”

REFERENCES

- [1] G. Tsagaropoulos, A. Eisenberg. *Macromolecules* 1995, 28, 396.
- [2] A. Yim, R. S. Chahal, L. E. St Pierre. *J. Colloid Interface Science* 1973, 43, 583.
- [3] H. Zou, S. Wu, J. Shen. *Chem. Rev.* 2008, 108, 3893.
- [4] V. Arrighi, I. J. McEwen, H. Qian, M. B. Serrano Prieto. *Polymer* 2003, 44, 6259.
- [5] T. von Werne, T. E. Patten. *J. Am. Chem. Soc.* 2001, 123, 7497.
- [6] J. Pyun, S. Jia, T. Kowalewski, G. D. Patterson., K. Matyjaszewski. *Macromolecules* 2003, 36, 5094.
- [7] K. Min, K. Matyjaszewski. *Macromolecules* 2005, 38, 8131.
- [8] C. Bartholome, E. Beyou, E. Bourgeat-Lami, P. Chaumont, F. Lefebvre, N. Zydowicz. *Macromolecules* 2005, 38, 1099.
- [9] C. Triebel, P. Kunzelmann, M. Blankenburg, H. Münstedt. *Polymer* 2011, 52, 3621.
- [10] E. Kontou and G. Anthoulis, *J. Appl. Polym. Sci.*, 2007, 105, 1723.
- [11] N. Jouault, P. Vallat, F. Dalmás, S. r. Said, J. Jestin and F. o. Boué, *Macromolecules* 2009, 42, 2031.
- [12] A. S. Sarvestani and C. R. Picu, *Polymer* 2004, 45, 7779.
- [13] M. A. Ver Meer, B. Narasimhan, B. H. Shanks, S. K. Mallapragada, *Acs Appl. Mater. Interfaces* 2010, 2, 41.
- [14] C. Bartholome, E. Beyou, E. Bourgeat-Lami, P. Cassagnau, P. Chaumont, L. David and N. Zydowicz, *Polymer* 2005, 46, 9965.
- [15] G. Havet, A. I. Isayev. *Rheol. Acta* 2003, 42, 47.
- [16] A. S. Sarvestani and C. R. Picu, *Polymer* 2004, 45, 7779
- [17] B. J. Ash, R. W. Siegel and L. S. Schadler, *J. Polym. Sci., Part B: Polym. Phys.* 2004, 30, 254.
- [18] R. Kotsilkova, D. Fagiadakis and P. Pissis, *J. Polym. Sci., Part B: Polym. Phys.* 2005, 43, 522.
- [19] Y. Y. Sun, Z. Q. Zhang, K. S. Moon, C. P. Wong, *J. Polym. Sci., Part B: Polym. Phys.* 2004, 42, 3849.
- [20] A. Kraft, V. Arrighi, P. M. E. Adams, K. Karotsis, A. McAnaw, I. J. McEwen, L. Ragupathy, C. Waring, *Polym. Prepr.* 2007, 48, 203.
- [21] P. S. Thomas, S. Thomas, S. Bandyopadhyay, A. Wurm, C. Schick, *Compos. Sci. Technol.* 2008, 68, 3220.
- [22] P. Antoni, D. Nyström, E. Malmström, M. Johansson, A. Hult, *Polym. Prepr.* 2005, 46(1), 477
- [23] R. Y. Hong, H. P. Fu, Y. J. Zhang, L. Liu, J. Wang, H. Z. Li and Y. Zheng, *J. Appl. Polym. Sci.* 2007, 105, 2176.
- [24] P. Akcora, S. K. Kumar, V. Garcia Sakai, Y. Li, B. C. Benicewicz and L. S. Schadler, *Macromolecules* 2010, 43, 8275.
- [25] M. A. Ver Meer, B. Narasimhan, B. H. Shanks and S. K. Mallapragada, *Acs Appl. Mater. Interfaces* 2010, 2, 41.
- [26] A. Kraft, V. Arrighi, N. Grima, *Polym. Mater. Sci. Eng.* 2008, 98, 687.