

Synthesis, Structure and Properties of Polymer Nanocomposites

M. Khlifa^{*}, A. Youssef, A. F. Zaed, M. Almakki
Department of Chemistry, Sebha University, Sebha, Libya
^{*}Corresponding Author: khelifa72@yahoo.co.uk

Abstract

A series of styrene-acrylonitrile (SAN) copolymer nanoparticles were prepared by grafting styrene-acrylonitrile from both aggregated silica and colloiddally dispersed silica nanoparticles using atom-transfer radical polymerisation (ATRP) in mini emulsion system. The grafted polymer silica nanoparticles were characterised using transmission electron microscopy (TEM), and gel permeation chromatography (GPC). The thermal and physical ageing behaviour of the nanocomposites have been examined by differential scanning calorimetry (DSC). The addition of silica nanoparticles to PSAN can influence its thermal and aging properties. Grafting PSAN-aggregated silica revealed considerable increase in the glass transition temperature, whereas colloiddally silica nanoparticles showed only a marginal improvement. Additionally, while dispersing PSAN in colloiddal and aggregated silica accelerated physical ageing, grafting to aggregated silica significantly reduced ageing rates.

Keywords: Poly (styrene-co-acrylonitrile); silica nanoparticles; physical ageing.

1. Introduction

Polymer materials are used in everything from packaging to airplanes and medical applications. However, homo-polymers often do not have the required properties for certain purposes. A technique that is commonly used in industry to adjust polymer properties is adding a filler material to the polymer, which can drastically affect its performance. Inorganic fillers such as silica are used extensively in many applications [1, 2] because they combine the advantages of the inorganic material, such as higher mechanical strength, with the flexibility and ductility of the organic polymers. The modification of polymer composites using sub-micrometer fillers with high surface-to-volume ratios is currently receiving a lot of interest in both academia and industry.

Growing polymer shells from inorganic nanoparticles has been researched extensively. One of the advantages of grafting over dispersing is that grafting allows for precise control over the interparticle distance due to the length of the polymer grafted

to it, which can affect some of the properties of the nanocomposite such as mechanical, electronic and optical properties [3].

The molecular weight (M_w) of a polymer grown from a nanoparticle can also be regulated by using a controlled polymerisation technique: polymerisations where the ability of the chains to terminate themselves has been greatly restricted. This means that the polymerisation continues until all the monomer has been polymerised, and thus the molecular weight of the product can be controlled by the monomer and initiator concentration.

Rühe first reported the attachment of polymers to silica nanoparticles using a surface-grafted azo initiator and a conventional radical polymerisation [3, 4]. More recently, controlled radical polymerisation have been used to generate surface-grafted polymer chains. The most prominent is atom-transfer radical polymerisation (ATRP), which has the added advantage that the functionalisation of silica particles with suitable initiator is straightforward and allows polymer chains to be grown from the silica

surface in a narrow size distribution. In contrast, nitroxide-mediated polymerisation 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 [5-7]. Fillers affect the mobility, and thus the T_g , of the polymer chains in the vicinity of the filler particle, and this effect is even more pronounced for the long term physical ageing properties of the polymer. The physical ageing of a material is an important issue to study, as it can lead to degradation of mechanical properties and strength, optical or transport properties which makes the materials much less useful for its intended application. While various characterisation techniques such as DSC, creep, fluorescence, and dielectric have been used to investigate physical aging in amorphous polymers [8, 9] very few studies have been reported on polymer-silica nanocomposites. 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 long-term ageing properties of nanocomposites made using both types of silica [10, 11]. Since the type of silica particles is known to significantly influence the properties of the polymer composites it is instructive to carry out comparative studies [12].

2. Material and Methods

2.1. Reagents

Commercial PSAN (25.6 wt% AN) used in dispersed nanocomposites was provided by Sigma-Aldrich; ascorbic acid and triethylamine from Lancaster; styrene (>99%), acrylonitrile (>99%), copper(II) chloride (+99%), copper(II) bromide (+99%), 3 aminopropyltriethoxysilane, anisole, tin(II) 2-ethylhexanoate ($\text{Sn}(\text{EH})_2$) and hexadecane from Aldrich. 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 nm were obtained from Cabot and a 30% solution MEK-ST Colloidal silica, having a particle size between 10-15 nm from Nissan Chemical.

2.2. Samples preparation

2.2.1. Preparation of PSAN-silica composites by dispersion

A 5% solution of PSAN in THF along with the required amounts of dried filler particle 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 for 48 hours. Samples were dried in an oven at $160 \text{ }^\circ\text{C}$ for 24 hours to remove all solvent residues.

2.2.2. 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 $40 \text{ }^\circ\text{C}$ 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, $205 \text{ }^\circ\text{C}/0.4 \text{ mbar}$) to yield product as a colourless liquid.

2.2.3. Synthesis of trichloroethyl carbamate-functionalised silica nanoparticles

Silica nanoparticles were dried at $110 \text{ }^\circ\text{C}/0.03 \text{ mbar}$ 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 $110 \text{ }^\circ\text{C}$ for 12 hours. The solid was centrifuged (4000 rpm, 20 min) and the supernatant decanted. Centrifugation-decantation was repeated 3 times using THF as the extracting solvent. The gel layer was transferred into a pre-weighed beaker and dried in an oven at $60 \text{ }^\circ\text{C}$ overnight.

2.2.4. Synthesis of poly(styrene-co-acrylonitrile) grafted onto silica

Initiator modified silica nano particles (0.20 g, 18.8 μmol ; 0.047 Br/g SiO_2) were dispersed in anisole (6 mL) with stirring for 12 hours in a Schlenk flask. Styrene (2.44 mL, 21.3 mmol) and acrylonitrile (0.82 mL, 12.5 mmol) were added, and then a solution of CuCl_2 (0.21 mg, 0.94 μmol), Me_6TREN (0.390 μL , 0.94 μL) complex in anisole (0.75 mL) was added. The mixture was degassed by three freeze-pump-thaw cycles. A solution of $\text{Sn}(\text{EH})_2$ (5.00 μL , 15.41 μmol) and Me_6TREN (6.50 μL , 15.4 μmol) in anisole (0.5 mL) was added. The Schlenk flask was then transferred into a thermostatic oil bath at $90 \text{ }^\circ\text{C}$. The reaction was stopped after 72 hours by exposing the catalyst to air. The product was precipitated into methanol (700 mL) over 30 minutes then

the supernatant removed by filtration. The precipitated was dried in a vacuum oven at 60 °C. The process was repeated several times with doubled amounts and with colloidal and aggregated silica initiator particles to collect several samples.

3. Results and Discussion

3.1. Copolymer synthesis

The grafting of SAN from the surface of silica nanoparticles was achieved first by attaching an ATRP initiator to the surface of the silica nanoparticles and then growing the chain from the modified silica surface. Initially, ATRP in miniemulsion was attempted with a mixture of styrene and acrylonitrile. However, mini-emulsion is carried out in water, and acrylonitrile is relatively soluble in water [13]. Thus water was replaced with anisole as shown in the literature [14], keeping the styrene and acrylonitrile mixed together so that polymerisation can take place. The polymerisation of SAN is also expected to be relatively slow, thus the reaction was allowed 72 hours to obtain a good yield of product with a sufficient M_w . The monomer feed was close to the azeotropic composition (ca. 63 mol% styrene and 37 mol% acrylonitrile), and copolymerisation was conducted in the presence of catalyst system in anisole as described in Figure 3.1. ATRP was conducted with 2-bromoisobutyryl amide or trichloroethyl-carbamate functionalised silica as initiators, $\text{Me}_6\text{TREN}/\text{Cu}(\text{II})$ as the catalyst, and an organic-soluble tin salt for reducing $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ instead of ascorbic acid in anisole at 90 °C. The reason for using tin(II) 2-ethylhexanoate ($\text{Sn}(\text{EH})_2$) is because ascorbic acid is not soluble in anisole. $\text{Sn}(\text{EH})_2$ was successfully used as the reducing agent in ATRP polymerisation, with different monomers such as butyl acrylate, styrene, methyl methacrylate and acrylonitrile [15-17]. The amounts of catalyst were varied to define the optimum conditions for control of SAN polymerisations. Three different amounts of $\text{Cu}(\text{II})$ were used 0.50, 1.00, and 2.00 equiv *vs.* $\text{Sn}(\text{EH})_2$. An organic reducing agent, glucose, was also examined for the ATRP of SAN to reduce the absolute amount of any metals in an ATRP process. Glucose has the advantage that it is soluble in polar solvents and environmentally benign. However, using glucose as reducing agent no polymerisation of SAN was observed. This result could be due to the added amount of glucose not being enough to initiate the polymerisation. The polymerisation was finished

by opening the flask and exposing the catalyst to air after 50 h. The product was further purified by extensive Soxhlet extraction with THF to remove free, unattached polymer. The nanocomposite was obtained in a yield of typically 65%, corresponding to about 2 g of nanocomposites. To obtain a consistent copolymer composition and different silica content, the synthesis was repeated several times using the same amounts of reagents with different amount of initiator-modified silica nanoparticles. In all cases, azeotropic feed ratio of acrylonitrile and styrene (37:63 molar ratios) was used. A reliable copolymer composition is important as it affects properties such as thermal and mechanical properties of the copolymer. Furthermore, selective TEM images of grafted PSAN silica particles are shown in Figure 3.2. The TEM image clearly demonstrates that a good dispersion of particles in the polymer matrix was observed.

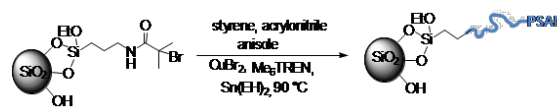


Figure 3.1: Synthetic scheme for the surface-initiated polymerisation of styrene/acrylonitrile from silica nanoparticles.

3.2. Thermal properties – glass transition temperature

The measured glass transition temperatures for the PSAN copolymer and the nanocomposites are shown in Figure 3.3. The T_g values of PSAN-Cab-o-sil H5 composites seem to be slightly lower than the T_g of neat PSAN although there is a change in the T_g between the various composites containing 9.5 wt%, 12.7 wt% or 20 wt% of silica. This result was also found with all PSAN-MEK-ST composites. Overall, it seems that adding silica nanoparticles has little effect on the glass transition temperature of PSAN. This is consistent with some of the literature reports which showed only a small decrease in the glass transition of the PSAN nanocomposites [18]. A plasticising residue, such as solvent residues, can also affect the T_g . This is an important factor to be considered in the dispersed samples as they are prepared by dissolving the polymer in THF, which is difficult to remove from the sample.

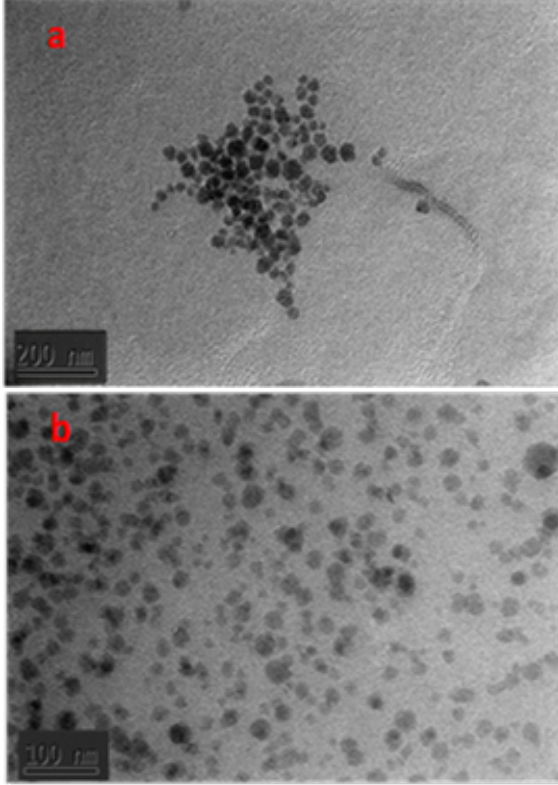


Figure 3.2: TEM images of (a) PSAN-Cab-o-sil H5 (20.0 wt%) and (b) PSAN-MEK-ST (20.0 wt%). The average diameter of the silica particles is 22 nm for Cab-o-sil H5 and 18 nm for MEK-ST.

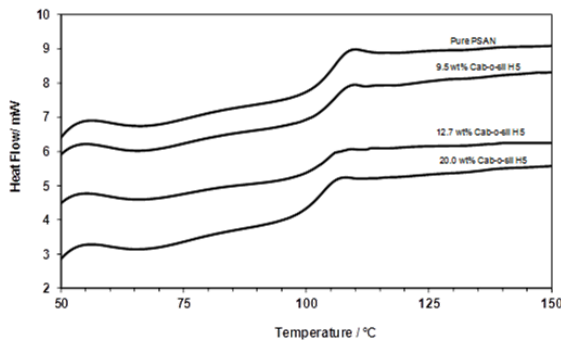


Figure 3.3: DSC traces of PSAN-grafted Cab-o-sil H5 composites. The traces have been shifted vertically for clarity.

3.3. Enthalpy relaxation

Enthalpy relaxation experiments are used to measure the effects of physical ageing on a polymer material. Physical ageing is a slow process of an amorphous material relaxing into its thermodynamic equilibrium

state when stored below the glass transition temperature [19]. This phenomenon is due to a series of small relaxation events taking place in the amorphous region of glassy polymers. Whilst the chemical structure of the polymer remains unchanged, the change in the packing of the polymer chains leads to a loss of thermodynamic properties such as enthalpy and entropy [20] which typically results to decreased thermal and mechanical properties over time. Several models have been proposed to analyse the experimental data collected by enthalpy relaxation experiments using differential scanning calorimetry (DSC).

A semi-empirical model proposed by Cowie and Ferguson (C-F) [21, 22] used in this paper to describe the physical ageing data of the polymer nanocomposites. At any ageing temperature (T_a) and ageing time (t_a), the enthalpy relaxed $\Delta H(T_a, t_a)$ is the integrated difference between the C_p curves for the aged and the unaged sample. According to CF, this is described by the following expression:

$$\Delta H(t_a, T_a) = \Delta H(\infty, T_a)[1 - \phi(t_a)] \quad (3.1)$$

where ΔH_∞ is the equilibrium excess enthalpy lost after an infinite ageing time and $\phi(t_a)$ is the Kohlraush-Williams-Watt (KWW) function, as follows:

$$\phi(t_a) = \exp\left\{-\left(\frac{t}{t_c}\right)^\beta\right\} \quad (3.2)$$

where β is related to the width of the distribution of relaxation times and t_c may be regarded as an ‘average’ relaxation time, i.e. both are kinetic parameters.

The C-F parameters of net PSAN and PSAN nanocomposites obtained from the fitted curves are listed in Table 3.1. The $\Delta H_\infty(T_a)$ data shows that the dispersed samples show a small decrease in the relaxed enthalpy at the plateau compared to pure PSAN. However, a significant decrease in relaxed enthalpy is shown in the grafted samples.

The β values give the distribution of relaxation times; a small value implies larger distribution. In general, the grafted Psan-Cab-o-sil H5 sample show lower β values than pure PSAN and the rest of the PSAN nanocomposites which could be due to a higher degree of interaction [23] between the particles and the polymer.

4. Conclusion

Using an ATRP procedure, PSAN was successfully grafted from aggregated and non-aggregated silica

Table 3.1: CF Parameters for PSAN and PSAN silica nanocomposites.

Polymer	T_a (K)	$T_g - T_a$ (K)	$\Delta H(T_a)$ (J g ⁻¹)	$\log t_c$ (min)	β
PSAN	376	15	1.88	2.21	0.45
	382	9	1.69	1.20	0.35
	386	5	0.91	1.65	0.40
PSAN-dispersed Cab-O-Sil (20 wt%)	372	15	1.82	2.48	0.44
	378	9	1.43	1.82	0.44
	382	5	0.98	1.56	0.42
PSAN-dispersed MEK-ST (20 wt%)	376	15	1.63	2.25	0.48
	382	9	1.41	1.98	0.30
	386	5	0.90	1.54	0.41
PSAN-grafted Cab-O-Sil (20 wt%)	384	15	1.05	1.96	0.39
	390	9	1.00	1.87	0.26
	394	5	1.54	1.58	0.36
PSAN-grafted MEK-ST (20 wt%)	380	15	1.26	1.89	0.54
	385	9	1.06	1.69	0.44
	390	5	0.48	1.65	0.48

nanoparticles. The addition of silica nanoparticles was found to increase the modulus and significantly lower the high-temperature damping in these composites, as can be seen from the tan delta *vs.* temperature plot. The attachment of the polymer to silica nanoparticles was particularly effective in improving the thermal and mechanical properties even further.

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