This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

www.rsc.org/softmatter
Particle-size Dependent Melt Viscosity Behavior and Properties of Three-arm Star Polystyrene/Fe$_3$O$_4$ Composites

Haiying Tan, a,b Yichao Lin, a,b Jun Zheng, a,b Jiang Gong, a,b Jian Qiu, a Haiping Xing, a,* Tao Tang a,*

The melt viscosity of three-arm star polystyrene (S3PS)/Fe$_3$O$_4$ nanoparticle composites was studied by means of rheological measurements. The arm molecular weight ($M_a$) of S3PS (or radius gyration) and particle size of Fe$_3$O$_4$ (radius ($R_p$): 3 nm and 44 nm) showed a strong influence on the melt viscosity behavior (at low shear frequencies) of S3PS/Fe$_3$O$_4$ composites. The reinforcement (viscosity increase) was observed in the composites where the $M_a$ was higher than the $M_c$ of PS ($M_c$: the critical molecular weight for chain entanglement). For $M_a < M_c$, when the size of Fe$_3$O$_4$ nanoparticle was changed, the melt viscosity of the composites exhibited either plasticization (melt viscosity reduction) or reinforcement. When the content of Fe$_3$O$_4$ was low (1 wt%), the transformation from plasticization to reinforcement behavior could be observed, which strongly depended on the size ratio of the radius of gyration ($R_g$) for S3PS to the size of nanoparticles ($R_p$). In addition, magnetic properties and thermal stability of S3PS/Fe$_3$O$_4$ composites were studied.

Introduction

Recently it has been found that the assembly of spherical nanoparticles in polymer matrices causes the reduction of melt viscosity. 1–5 This phenomenon is in contradiction with the expression derived from Einstein, 6 describing the increase of the viscosity as a function of the volume fraction of fillers in a matrix. Mackay’s group 1–3 has found that polymer molecular weight ($M_w$), radius of gyration ($R_g$) and nanoparticle radius ($R_p$), are key structural factors affecting the dispersion states of nanoparticles. 7 The critical molecular weight for entanglement ($M_c$) designates where a viscosity reduction is possible. 2,7 The average interparticle half-gap ($h$) and the ratio of $R_g$ to $R_p$ are also important for a viscosity decrease to occur. The $h$ can be calculated from the following relationship:

$$h/R_g = [\phi_m/\phi]^{1/3} - 1$$  

(Equation 1)

where $\phi_m$ is the maximum random packing volume fraction (~0.638), $\phi$ is the volume fraction of nanoparticles. Twice of this distance is the average distance separating particles. According to the results from Mackay group, 1–3 viscosity reduction just happened when molecular weight of polymer was larger than the entanglement molecular weight and the $h$ was smaller than $R_g$. Recently, a lot of attention has been paid on this phenomenon coming up with controversial observations and explanations. 1–5,8–14 The possible mechanisms for the reduction of melt viscosity of polymer/nanoparticle composites include dilution of the entanglement density of polymer chains, increased excluded free volume induced around the nanoparticles, 8 selective adsorption of high molecular weight polymer chains, 15 slip between sample and geometry during rheological testing, 2 constraint release of entangled polymer chain, 15,14 and degradation of polymer. 16,17

So far the reduction of melt viscosity induced by the addition of the nanoparticles has been found in linear polymer matrix. Very recently, we have found that the presence of well-dispersed C$_{60}$ nanoparticles reduces the viscosity of star polystyrene (SPS) melts when the arm molecular weight ($M_a$) of SPS is smaller than the $M_c$ of PS. 18 However, the viscosity increases when the $M_a$ is higher than $M_c$. The incorporation of POSS also decreases the melt viscosity of the unentangled SPS, and reinforces the polymer matrix when $M_a$ is higher than $M_c$. 19, although the interaction between POSS and SPS is different from that between C$_{60}$ and SPS. Importantly the $R_g$s of both C$_{60}$ and POSS are smaller than the $R_g$ of SPS. Mackay’s group studied the dependence of melt viscosity on the nanoparticle size and the average interparticle half-gap ($h$) in linear PS (LPS). They found that larger particle sizes will not produce melt viscosity decreased behaviour in entangled LPS. 1 However, there is no report studying the effects of the sizes of nanoparticles on the melt behavior of star polymer/nanoparticle systems.

In this work, following our previous study, two kinds of magnetic Fe$_3$O$_4$ nanoparticles with different diameters were used to explore the influence of the size of nanoparticles on the melt behavior of SPS/Fe$_3$O$_4$ composites. Magnetic polymer composites have attracted much attention because of their intriguing properties. 20–24 The required properties to magnetic
nanoparticles for many applications are narrow nanosized distribution, high and uniform magnetic content and high saturation magnetization ($M_s$). Different applications require them to have different sizes. Owing to the need of applications, various methods were established to synthesize different sized Fe$_3$O$_4$. The two sizes of Fe$_3$O$_4$ were synthesized using the reported methods. The dependence of melt viscosity of SPS/Fe$_3$O$_4$ composites on the $M_w$ and $R_g$ of SPS, the $R_p$ of nanoparticle and the average interparticle half-gap ($h$) was studied. Also the influence of dispersed spherical nanoparticles in SPS matrix on thermal stability and magnetic performance of SPS was investigated.

**Experimental Section**

**Materials.** 1,3,5-tribromomethylbenzenes and copper bromide (CuBr, 99.999%) were purchased from Aldrich. 2,2'-Dipyridyl was purchased from TCI. Styrene (99%), toluene, tetrahyrofuran (THF), CH$_2$Cl$_2$, hexane, methanol, FeCl$_3$·6H$_2$O, oleic acid, ethylene glycol (EG), ethylenediamine (EN), sodium acetate (NaAc), and neutral alumina were purchased from China National Medicines Corporation Ltd. Fe(acac)$_3$, 1,2-hexadecanediol, phenyl ether and oleylamine were purchased from Acros. Styrene was distilled over CaH$_2$ prior to use. Toluene was purified by Braun system. All the other reagents were used as received. Three-arm star polystyrene (S3PS) was synthesized via ATRP technique. The details about the synthesis and characterization of S3PS samples were reported in our previous report. Table 1 shows molecular parameters of a series of S3PS samples.

**Synthesis of nano-Fe$_3$O$_4$ (6 nm, named Fe(3)).** Fe$_3$O$_4$ nanoparticles with the diameter of 6 nm were prepared according to the method of Sun. Fe(acac)$_3$ (2 mmol), 1,2-hexadecanediol (10 mmol), oleic acid (6 mmol), oleylamine (6 mmol), and phenyl ether (20 mL) were mixed and magnetically stirred under a flow of nitrogen. The mixture was heated to 200 °C for 30 min and then, under a blanket of nitrogen, heated to reflux (280 °C) for another 30 min. The black-brown mixture was cooled to room temperature by removing the heat source. Under ambient conditions, ethanol (40 mL) was added to the mixture, and a black material was precipitated and separated via centrifugation. The black product was dissolved in hexane in the presence of oleic acid (0.05 mL) and oleylamine (0.05 mL). Centrifugation (6500 rpm, 10 min) was applied to remove any undispersed residue. The product (Fe$_3$O$_4$ nanoparticles) was then precipitated with ethanol, centrifuged (6500 rpm, 10 min) to remove the solvent, and redispersed in hexane.

**Synthesis of nano-Fe$_3$O$_4$ (88 nm, named Fe(44)).** For the synthesis of 100 nm Fe$_3$O$_4$ nanoparticles, FeCl$_3$·6H$_2$O (2.50 g) was injected into a mixture containing 8.9 mL EN and 80 mL EG under magnetic stirring, followed by the addition of NaAc (5.00 g). The mixture was transferred to a Teflon-lined stainless-steel autoclave and sealed, to heat at 210 °C for 6 h. The produced magnetite nanoparticles were washed with deionized water. The product, Fe$_3$O$_4$ nanoparticles with the diameter of 88 nm, was separated using a magnet, and finally dried in an oven at 80 °C for 12 h. This method was reported previously.

**Preparation of SPS/Fe$_3$O$_4$ composites.** Fe$_3$O$_4$ was dissolved in toluene at a concentration of 2 mg/mL by ultrasonication. Next, a certain amount of Fe$_3$O$_4$/toluene solution was added to SPS/toluene solution to obtain the desired weight fractions of Fe$_3$O$_4$ in the final composite. The mixed solutions were dispersed by ultrasonication and then added drop-wise into a large volume of methanol to get co-precipitation of SPS and Fe$_3$O$_4$. The solids were filtered from methanol and dried in vacuum at 80 °C for more than 24 h to remove the solvent. The symbol S3PS-x-Fe(y)-z represents three-arm star polystyrene/Fe$_3$O$_4$ composites, where $x$ is the molecular weight of S3PS, $y$ represents the diameter (nm) of Fe$_3$O$_4$ nanoparticles and weight fraction of $z$ Fe$_3$O$_4$. To our best knowledge, large concentrations of particles will lead to aggregation, so the weight fraction of Fe$_3$O$_4$ in the polymer matrix was only 1 wt%.

**Characterization.** Dispersion state of the obtained SPS/Fe$_3$O$_4$ composites was observed by transmission electron microscopes (TEM, JEOL1011 JEOL, Japan) and high resolution transmission electron microscope (Teccni G2 F20 FE-TEM, FEI, Holland) on microtome sections at 100 kV and 200 kV accelerating voltage, respectively. Ultrathin sections were cut on Leica Ultracut using a glass knife at room temperature. The samples were collected on carbon-coated copper TEM grids. The glass transition temperature ($T_g$) of samples was measured by differential scanning calorimetry (DSC, Mettler Toledo DSC 1, Switzerland). Samples of about 10 mg were loaded in aluminum pans and heated at a rate of 10 °C min$^{-1}$ under nitrogen atmosphere. A first scanning was carried out from room temperature to 200 °C and the samples were held for 3 min at this temperature to erase previous unknown thermal history. Then the samples were cooled down to ambient temperature and a second heating scan was carried out heating up to 200 °C. The temperature corresponding to the midpoint in the heat capacity step-rise was used for the determination of $T_g$.

**Results and discussion**

**Morphology of S3PS/Fe$_3$O$_4$ composites.** Fig. 1 shows the TEM images of synthesized Fe$_3$O$_4$ nanoparticles (Fe(3) and...
Fe(44)) and their size distribution histograms. The average radiiuses of Fe(3) and Fe(44), measured by Nano Measurer 1.2, were 3.2 and 43.7 nm, respectively. Based on the preparation method, the synthesised Fe3O4 was decorated by organic group as shown in Fig. S1. The size distribution of Fe(3) was narrower than that of Fe(44), which was caused by the different preparation methods. Fig. 1b was the HR-TEM image of Fe(3). The morphologies of SPS/Fe3O4 composites were shown in the SI (Fig. S2). Most of both the particles could be dispersed in the matrices of S3PS-48k and S3PS-150k, although some of them formed aggregates. Considering their different sizes of the two particles, there was no obvious difference in the dispersion states.

![Fig. 1. Morphology of Fe3O4 synthesized by the two different methods. (a) TEM image of Fe(3) observed by TEM with the accelerate voltage at 100 kV; (b) TEM image of Fe(3) observed by HR-TEM with the accelerate voltage at 200 kV; (c) TEM image of Fe(44) observed by TEM with the accelerate voltage at 100 kV; size distribution of (d) Fe(3) and (e) Fe(44) was measured by Nano Measurer 1.2, respectively.](image)

The effect of particle sizes on the melt viscosity. The influence of the added Fe3O4 on the melt behavior of S3PS was studied by linear oscillatory frequency sweep experiments. Fig. 3a shows the plots of complex viscosity ($\eta^*$) versus angular frequency ($\omega$) for S3PS-18k containing Fe3O4 nanoparticles with two different sizes. The $R_g$ of S3PS-18k (3.1 nm) was very close to the $R_p$ (3.2 nm) of Fe(3) and smaller than that of Fe(44). Compared to pure S3PS-18k, the addition of these two Fe3O4 increased the $\eta^*$ at low frequencies of S3PS-18k matrix. The changing trends of $G'$ and $G''$ were similar to those of complex viscosity for S3PS-48k, S3PS-75k and their composites with Fe3O4 of two sizes (Fig. S4 and S5). Although the $M_s$ of S3PS-18k, S3PS-48k and S3PS-75k were smaller than the $M_c$ of PS, the changing trends in the $\eta^*$ of their composites were different, resulting from the different ratio of the $R_g$ to the $R_p$ of Fe3O4 nanoparticles. When the $M_c$ of SPS was higher than the $M_c$ of Fe3O4, the incorporation of Fe(3) or Fe(44) increased the viscosity of polymer matrix (Fig. 2d), no matter what the ratio of $R_p$ to $R_g$ was. Because the $R_g$ of S3PS-150k was 13.5 nm, higher than $R_p$ of Fe(3) but lower than $R_p$ of Fe(44). The changing trends in $G'$ and $G''$ for S3PS-150k and its composites with Fe(3) and Fe(44) were given in Fig. S6.

According to the summary made by Mackay group,$^3$ for a viscosity reduction in linear polymer composites: the polymer must be entangled ($M_s > M_c$), the radius of nanoparticle and the average interparticle half-gap ($h$) must be less than the $R_p$ of polymer matrix. In this work, the radius of Fe(3) and Fe(44) ($R_g$) were 3.2 and 43.7 nm, respectively. The $R_p$ of Fe(44) was larger than the $R_p$ of all the synthesized S3PS (2.9–13.5 nm), but the $R_p$ of Fe(3) was in between the $R_p$ of the synthesized SPS, depending on the molecular weight of S3PS matrix. The value of interparticle half-gap ($h$) can be determined from the Equation 1 in the introduction part. In the samples with 1 wt% Fe3O4, the $h$ is 18.5 nm and 253.1 nm for Fe(3) and Fe(44) system, respectively. This shows that $h$ values of both particles in S3PS/Fe3O4 composites are larger than the $R_g$ of all the synthesized S3PS (2.9–13.5 nm) (see Table 1), including the S3PS samples with $M_c < M_s$ and $M_c > M_s$. However, from the results in Fig. 2, different changing trend in complex viscosity was observed in the S3PS/Fe3O4 composites. For example, the incorporation of Fe(3) increased the complex viscosity of S3PS-18k and S3PS-150k, but decreased the viscosity of S3PS-48k and S3PS-75k. So we guess that the Mackay’s assumption that $h$ must be lower than $R_p$, is not valid in this system. There are several other factors that might be responsible for the viscosity change in polymer matrix, which will be discussed in the later section.

To confirm the results about the changing trend of melt viscosity from linear frequency sweep measurements, flow sweep mode was also used in the rheological measurements. S3PS-48k and S3PS-150k were used as examples to show the changing trend of shear viscosity ($\eta$) versus shear rate ($\gamma$). As shown in Fig. 3, S3PS-48k, S3PS-150k and their composites exhibit a Newtonian plateau region at low shear rate. The zero shear viscosity ($\eta_0$) could be directly obtained from the plateau at the lowest shear rate. The results of other samples were given in the SI (Fig. S7). Table 2 shows the $\eta_0$ of four kinds of S3PS and their composites with Fe3O4. The incorporation of Fe(3) increased the shear viscosity of S3PS-48k, but the presence of Fe(44) increased that of S3PS-48k (Fig. 3a). In contrast, the addition of both Fe(3) and Fe(44) increased the viscosity of S3PS-150k (Fig. 3b). The larger the particle size, the higher the shear viscosity. The changing trend of shear viscosity for S3PS/Fe3O4 composites was similar to that of complex viscosity of all the samples. On using the data of linear oscillatory frequency sweep experiments and steady shear rheology, Cox–Merz rules was tried. The so called Cox–Merz rule describes the relationship between complex viscosity and shear viscosity as:

$$\eta^* (\omega) \bigg|_{\omega \rightarrow 0} = \eta (\gamma) \bigg|_{\gamma \rightarrow 0} \quad \text{(Equation 2)}$$

But for some of the samples it failed, e.g. S3PS-150k-Fe(44), which results from the aggregation formed (Fig S2d). The failure of the Cox–Merz rule for these composites (while being
obeyed for the polymer itself) suggests aggregates formed in the composites. In SPS/Fe$_3$O$_4$ composites, the formation of large aggregates was responsible for the failure of this rule.

Fig. 2. Complex viscosity ($\eta^*$) vs angular frequency ($\omega$) for (a) S3PS-18k, (b) S3PS-48k, (c) S3PS-75k, (d) S3PS-150k and their composites with two different sizes of Fe$_3$O$_4$ at 150 °C.

Table 2. The glass transition temperature ($T_g$), plateau modulus ($G_N^0$), apparent relaxation time ($\tau_a$), zero shear viscosity ($\eta_0$) and $\eta^*_{0.05}$ for pure S3PS and their composites with Fe$_3$O$_4$ nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>$G_N^0$ (MPa)</th>
<th>$\tau_a$ (s)</th>
<th>$\eta_0$ (Pa·s)</th>
<th>$\eta^*_{0.05}$ (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3PS-18k</td>
<td>99.2±0.3</td>
<td>--</td>
<td>--</td>
<td>3100±100</td>
<td>2900±100</td>
</tr>
<tr>
<td>S3PS-18k-Fe(3)</td>
<td>102.3±0.1</td>
<td>--</td>
<td>--</td>
<td>13100±600</td>
<td>9780±400</td>
</tr>
<tr>
<td>S3PS-18k-Fe(44)</td>
<td>102.2±0.2</td>
<td>--</td>
<td>0.006</td>
<td>40800±1600</td>
<td>20100±400</td>
</tr>
<tr>
<td>S3PS-48k</td>
<td>101.9±0.3</td>
<td>0.22±0.02</td>
<td>0.045</td>
<td>38900±1200</td>
<td>25800±900</td>
</tr>
<tr>
<td>S3PS-48k-Fe(3)</td>
<td>103.4±0.4</td>
<td>0.22±0.04</td>
<td>0.043</td>
<td>28800±1100</td>
<td>22700±1100</td>
</tr>
<tr>
<td>S3PS-48k-Fe(44)</td>
<td>103.6±0.2</td>
<td>0.16±0.01</td>
<td>0.074</td>
<td>47700±1000</td>
<td>38900±1200</td>
</tr>
<tr>
<td>S3PS-75k</td>
<td>104.1±0.2</td>
<td>0.17±0.01</td>
<td>0.242</td>
<td>55800±2700</td>
<td>55100±1100</td>
</tr>
<tr>
<td>S3PS-75k-Fe(3)</td>
<td>103.9±0.1</td>
<td>0.19±0.03</td>
<td>0.203</td>
<td>38900±1400</td>
<td>47200±1500</td>
</tr>
<tr>
<td>S3PS-75k-Fe(44)</td>
<td>103.5±0.3</td>
<td>0.15±0.02</td>
<td>0.364</td>
<td>101200±3500</td>
<td>78000±2100</td>
</tr>
<tr>
<td>S3PS-150k</td>
<td>105.8±0.2</td>
<td>0.15±0.03</td>
<td>1.248</td>
<td>166500±2300</td>
<td>165000±2500</td>
</tr>
<tr>
<td>S3PS-150k-Fe(3)</td>
<td>105.1±0.3</td>
<td>0.13±0.02</td>
<td>3.096</td>
<td>379200±1800</td>
<td>251400±1100</td>
</tr>
<tr>
<td>S3PS-150k-Fe(44)</td>
<td>102.5±0.4</td>
<td>0.12±0.04</td>
<td>3.646</td>
<td>685500±1100</td>
<td>254400±1200</td>
</tr>
</tbody>
</table>

$^a$ The relaxation time was determined from the relationship: $\tau_a = 1/\omega_{cross}$, where $\omega_{cross}$ was the angular frequency where the storage modulus equals to loss modulus showed in Table S1.$^b$ Zero shear viscosity determined from the plateau region of steady state shear viscosity. $^c$ Complex viscosity at the frequency of 0.05 rad/s.
Fig. 3. Steady state shear viscosity as a function of shear rate for (a) S3PS-48k and (b) S3PS-150k and their composites with 1 wt% of Fe(3) and Fe(44) at 150 °C.

Fig. 4 shows the ratio of viscosity (η*<sub>0.05,C</sub> to η*<sub>0.05,P</sub>) as a function of R<sub>g</sub>/R<sub>p</sub>. For the composites containing both Fe(3) and Fe(44), when the arm molecular weight was smaller than the M<sub>c</sub>, the viscosity ratio decreased with the increase of R<sub>g</sub>/R<sub>p</sub>. However, it increased when the M<sub>a</sub> was higher than M<sub>c</sub>, although the R<sub>g</sub>/R<sub>p</sub> ratio became larger. The main difference in the viscosity ratio changing was that the viscosity ratio became lower than 1 when M<sub>a</sub> < M<sub>c</sub> and R<sub>g</sub>/R<sub>p</sub> > 1. It can be seen that the viscosity ratio depends on both the arm molecular weight and the R<sub>g</sub>/R<sub>p</sub> ratio.

From the oscillatory frequency sweep results, the plateau modulus (G<sub>N</sub>*) of a sample is obtained by the “MIN method”28.

\[ G_N^* = G'(\omega)_{\text{tan}\delta\rightarrow\text{min}} \]

where tanδ is the damping factor, and the value of G' at the minimum of tanδ is G<sub>N</sub>*. The apparent relaxation time (τ<sub>a</sub>) of the sample is calculated from the cross-over frequency (ω<sub>ω</sub>) of G' and G″ from the linear frequency sweep results (τ<sub>a</sub> = 1/ω<sub>ω</sub>).14 The G<sub>N</sub>*, τ<sub>a</sub> and η*<sub>0.05</sub> of the samples are summarized in Table 1. The changing trend of η*<sub>0.05</sub> of S3PS/Fe<sub>3</sub>O<sub>4</sub> composites was consistent with that of apparent viscosity (η<sub>a</sub>, η<sub>a</sub> = G<sub>N</sub>*, τ<sub>a</sub>)29. Owing to the low complex viscosity of S3PS-18k, the ω<sub>ω</sub> of the samples cannot be determined under the measured conditions. The addition of Fe(3) slightly decreased the τ<sub>a</sub> of S3PS-48k, but the presence of Fe(44) increased the τ<sub>a</sub> of S3PS-48k. The τ<sub>a</sub> of S3PS-75k showed a similar changing trend after incorporating Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The changing trend of τ<sub>a</sub> in both S3PS-48k and S3PS-75k matrices was similar to η*<sub>0.05</sub>. When the arm chain was entangled, the incorporation of both Fe(3) and Fe(44) increased the τ<sub>a</sub>. The changing trend of τ<sub>a</sub> for S3PS-150k was also similar to that of the complex viscosity. Thus the addition of Fe<sub>3</sub>O<sub>4</sub> affected the relaxation mode of S3PS. Generally speaking, the addition of Fe<sub>3</sub>O<sub>4</sub> decreased the G<sub>N</sub>* of S3PS/Fe<sub>3</sub>O<sub>4</sub> composites except the case of S3PS-75k-Fe(3). This result demonstrated that the addition of Fe<sub>3</sub>O<sub>4</sub> changed the chain relaxation mode of S3PS matrix to some extent. Larger particles will block the chain relaxation process.

To further study the relaxation process of S3PS/Fe<sub>3</sub>O<sub>4</sub> in large time scales, Fig. 5 shows the continuous relaxation spectra of S3PS-48k, S3PS-150k and their composites as examples. At a short time scale, the presence of Fe<sub>3</sub>O<sub>4</sub> did not significantly affect the Rouse or the plateau regime in the relaxation spectra of S3PS-48k or S3PS-150k. Instead, at a longer time scale, the incorporation of Fe<sub>3</sub>O<sub>4</sub> influenced the terminal region of the relaxation spectra of S3PS/Fe<sub>3</sub>O<sub>4</sub> composites. Compared to the relaxation behavior of pure S3PS-48k, the longest relaxation time of S3PS-48k-Fe(3) became shorter, while the longest relaxation time of S3PS-48k-Fe(44) became longer (Fig. 5a). In Fig. 5b, the longest relaxation times of S3PS-150k/Fe<sub>3</sub>O<sub>4</sub> composites were always longer than that of pure S3PS-150k matrix. These results were consistent with the changing trends of their melt viscosities at low shear frequencies (see Fig S4b and S4d). Thus, the incorporation of Fe<sub>3</sub>O<sub>4</sub> changed the relaxation mode of star PS chains. Large particles blocked the relaxation of S3PS chain, but small particles acted as lubricator that promoted the motion of the chains and resulted in decreased viscosity.

Discussion about the changing trends of melt viscosity of S3PS/Fe<sub>3</sub>O<sub>4</sub> composites. In our previous reports,18,19 the reduction of melt viscosity in the S3PS/C<sub>60</sub> (or POSS) system can be observed only in the S3PS matrix with low molecular weight (M<sub>a</sub> < M<sub>c</sub>) and the R<sub>g</sub> of S3PS was higher than R<sub>p</sub>. What will occur to the melt viscosity of S3PS when R<sub>g</sub> ≤ R<sub>p</sub>? Unfortunately, the diameters of C<sub>60</sub> (0.7 nm) and POSS (1.5 nm) are always smaller than the R<sub>p</sub> of all the synthesized SPS, and it is difficult to change the diameters of both them. So here we synthesize different sized Fe<sub>3</sub>O<sub>4</sub> to study the influence of the size of nanoparticles on melt viscosity of S3PS. In this work, the results showed that the values of M<sub>a</sub>, R<sub>g</sub> and R<sub>p</sub> determined the changing trend of melt viscosity for S3PS/Fe<sub>3</sub>O<sub>4</sub> system.
the cases with $M_\alpha < M_\epsilon$, when $R_\alpha > R_p$, the melt viscosity of S3PS/Fe$_3$O$_4$ (1 wt%) composites was lower than that of S3PS; however, when $R_\alpha \leq R_p$, the increased melt viscosity was observed in the S3PS/Fe$_3$O$_4$ system. When $M_\epsilon$ was higher than $M_\alpha$, in spite of the ratio of $R_\alpha$ to $R_p$, the incorporation of Fe$_3$O$_4$ increased the complex viscosity of S3PS. Compared to our previous reports, we find that in this work, when $R_\alpha \leq R_p$, the addition of Fe$_3$O$_4$ composites always increases the melt viscosity of S3PS in spite of the ratio of $M_\alpha$ to $M_\epsilon$. This can be explained by hydrodynamic reinforcement. The case of $R_\alpha \geq R_p$ is similar to forming aggregates of small nanoparticles (such as the cases containing high content of C$_{60}$ or POSS), which results in hydrodynamic reinforcement for polymer melt. This proves that the basic requirement ($R_\alpha > R_p$) for the appearance of the reduced melt viscosity is also necessary in the star polymer/nanoparticles composite.

In summary, there are several possible factors to influence the changing trend of melt viscosity in polymer/nanoparticles composites. Firstly, the topological structure was one of the main reasons for the dependence of melt viscosity of star polymer/nanoparticles system on the molecular weight of arms in star polymers. Owing to steric resistance, the nanoparticles can not enter the centre of star polymers, and most of nanoparticles are distributed the end regime of star polymers. So the topological structure of star polymer induces a more heterogeneous dispersion of nanoparticles in the star polymer matrix than the dispersion state of nanoparticles in the linear polymer matrix. Secondly, both $M_\alpha < M_\epsilon$ and $R_\alpha > R_p$ are the basic requirements for the appearance of the reduced melt viscosity in the star polymer/nanoparticle composites. Of course, the well-dispersed state of nanoparticles is also required. From the above results, it can be seen that the change of melt viscosity is only closely related to the relaxation time (Table 2), not to the $G''$ and glass transition temperature ($T_g$). As we know, the free volume is tied up with the $T_g$ of polymers. Generally, the increase of $T_g$ means the reduction of the free volume. The presence of Fe(3) or Fe(44) increased the $T_g$ of S3PS-48k, but the addition of Fe(3) decreased the melt viscosity of S3PS-48k, and the addition of Fe(44) led to the increase of melt viscosity of S3PS-48k. Comparing the changing trend of melt viscosity with that of $T_g$ in S3PS-75k and S3PS-150k before and after adding Fe$_3$O$_4$ nanoparticles, we also did not find their close relation.

**Magnetic properties.** The magnetic properties of S3PS/Fe$_3$O$_4$ composites were examined at 300 K via a superconducting quantum interface device (SQUID) magnetometer. As revealed in the hysteresis loops (Fig. 6), the field dependent magnetization plot illustrates that the S3PS/Fe$_3$O$_4$ composites are superparamagnetic at room temperature, since there is no hysteresis detected, and both remanence and coercivity are approximately zero. The saturation magnetization values of Fe(3) and Fe(44) were 77.1 and 65.9 emu g$^{-1}$, respectively. The saturation magnetizations of S3PS/Fe(3) and S3PS/Fe(44) were less than those of Fe$_3$O$_4$ nanoparticles. As shown in Fig. 6, the saturation magnetizations of S3PS-48k-Fe(3) and S3PS-48k-Fe(44) were 0.97 and 0.51 emu g$^{-1}$, respectively; and those of S3PS-150k-Fe(3) and S3PS-150k-Fe(44) were 0.79 and 0.34 emu g$^{-1}$, respectively. In the cases containing Fe(3), there are large aggregates formed in S3PS-150k matrix, so the saturation magnetizations for Fe$_3$O$_4$ endow S3PS matrix with magnetic properties.

**Table 3.** Summary of the TGA results (Fig. 7) for S3PS-48k, S3PS-150k and their composites with Fe(3) and Fe(44) under air atmosphere.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{5\text{wt%}}$ ($^\circ\text{C}$)</th>
<th>$T_{10\text{wt%}}$ ($^\circ\text{C}$)</th>
<th>$T_{\text{max}}$ ($^\circ\text{C}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3PS-48k</td>
<td>342</td>
<td>355</td>
<td>399</td>
</tr>
<tr>
<td>S3PS-48k-Fe(3)</td>
<td>354</td>
<td>370</td>
<td>416</td>
</tr>
<tr>
<td>S3PS-48k-Fe(44)</td>
<td>348</td>
<td>367</td>
<td>416</td>
</tr>
<tr>
<td>S3PS-150k</td>
<td>354</td>
<td>367</td>
<td>402</td>
</tr>
<tr>
<td>S3PS-150k-Fe(3)</td>
<td>368</td>
<td>377</td>
<td>418</td>
</tr>
<tr>
<td>S3PS-150k-Fe(44)</td>
<td>361</td>
<td>375</td>
<td>414</td>
</tr>
</tbody>
</table>

$^aT_{5\text{wt\%}}$ and $T_{10\text{wt\%}}$ are the temperature where 5 and 10 wt % weight loss occurred. $^bT_{\text{max}}$ equals to the temperature at which the maximum weight loss rate occurred.

**Thermal stability.** Fig. 7 presents TGA curves of S3PSs and their composites with Fe$_3$O$_4$ under air atmosphere. Detailed data are listed in Table 3. The temperature at 5 wt% weight loss ($T_{5\text{wt\%}}$) for S3PS-48k was lower than that of S3PS-150k, but the temperature for the maximum weight loss rate ($T_{\text{max}}$) of both S3PS-48k and S3PS-150k appears at $\sim$400 $^\circ$C, which is very close to that of linear PS. As for the S3PS-48k-Fe(3) composites, its $T_{5\text{wt\%}}$, $T_{10\text{wt\%}}$, and $T_{\text{max}}$ were 12, 15, and 17 $^\circ$C higher than those of pure S3PS-48k, indicating that the presence of Fe$_3$O$_4$ dramatically improved the thermo-oxidative stability of S3PS under air. As for Fe(44), similar changing trends in $T_{5\text{wt\%}}$, $T_{10\text{wt\%}}$ and $T_{\text{max}}$ were observed. When the molecular weight of S3PS was increased to 150k, the $T_{5\text{wt\%}}$, $T_{10\text{wt\%}}$ and $T_{\text{max}}$ of S3PS-150k-Fe(3) were 14, 10, 16 $^\circ$C higher than those of S3PS-150k. Similar changing trends in $T_{5\text{wt\%}}$, $T_{10\text{wt\%}}$ and $T_{\text{max}}$ of S3PS-150k-Fe(44) were also observed. The temperature for the maximum weight loss rate increased about 15 $^\circ$C under air atmosphere. From these results, it is evident that the thermo-oxidative stabilities of all the S3PS/Fe$_3$O$_4$ composites were improved comparing with that of pure S3PS.
matrix. Similar changing trend in S3PS-18k and S3PS-75k was observed.

![TGA and DTG curves of (a) S3PS-48k, (b) S3PS-150k and their composites with Fe(3) and Fe(44) under air atmosphere.](image)

**Fig. 7.** TGA and DTG curves of (a) S3PS-48k, (b) S3PS-150k and their composites with Fe(3) and Fe(44) under air atmosphere.

**Conclusions**

Compared to pure S3PS, the melt behaviour of S3PS/Fe$_3$O$_4$ composites strongly depended on the molecular weight of arm ($M_a$) and the size of Fe$_3$O$_4$ nanoparticles ($R_p$). The incorporation of Fe$_3$O$_4$ changed the relaxation model of the S3PS chains, in which the longest relaxation time changed with the complex viscosity. When $R_g \leq R_p$, the addition of small amount of Fe$_3$O$_4$ nanoparticles (1 wt%) resulted in the increase in the melt viscosity of S3PS/Fe$_3$O$_4$ composites, in spite of molecular weight of arm in star PS. The reduced melt viscosity was observed in the S3PS/Fe$_3$O$_4$ composites, where $M_a < M_c$ and $R_g > R_p$. Interestingly, in the case of S3PS with low molecular weight ($M_a < M_c$), there was the crossover from plasticization (viscosity reduction) to reinforcement behavior (viscosity increase) by adjusting the size ratio of $R_g$ of S3PS to nanoparticles size ($R_p$). This provides a new method to control melt behaviour of polymers. Furthermore, the addition of Fe$_3$O$_4$ nanoparticles also endowed the materials magnetic properties, and improved thermal stability of S3PS.

**Acknowledgements**

This work is financially supported by the National Natural Science Foundation of China for the Projects (51233005, 51073149 and 21304089).

**Notes and references**

* State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

* University of the Chinese Academy of Sciences, Beijing 100039, China

*Email: ttang@ciac.ac.cn; hpxing@ciac.ac.cn

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/


Particle-size Dependent Melt Viscosity Behavior and Properties of Three-arm Star Polystyrene/Fe$_3$O$_4$ Composites

Haiying Tan,$^{a,b}$ Yichao Lin,$^{a,b}$ Jun Zheng,$^{a,b}$ Jiang Gong,$^{a,b}$ Jian Qiu,$^a$
Haiping Xing,$^{a,*}$ Tao Tang$^{a,*}$

Compared to three-arm star polystyrene (S3PS), the melt viscosity of S3PS/Fe$_3$O$_4$ composites reduces (white area) or increases (yellow area), which strongly depends on arm molecular weight of S3PS ($M_a$), radius gyration of SPS ($R_g$) and the size of Fe$_3$O$_4$ nanoparticles ($R_p$).