

# Influence of the Particle Size on the Viscoelastic Glass Transition of Silica-Filled Polystyrene

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**ABSTRACT:** The effects of the filler particle size and volume fraction on the viscoelastic glass-transition temperature of filled polymers were investigated with polystyrene containing silica nanoparticles. The samples were prepared by a solution-mixing method to obtain a better dispersion of silica particles. Dynamic rheometry was used to study the viscoelastic behavior of these materials in the melt state. The addition of silica particles broadened the elastic modulus and increased its magnitude in the glass-transition region. Also, the magnitude of the loss modulus and loss tangent

peaks decreased. These phenomena were intensified by a reduction of the silica particle size, which increased filler–filler interactions. Furthermore, with a reduction in the size of the silica particles, the glass-transition temperature of the filled polymer increased simultaneously with an increase in the interfacial layer volume fraction, which was related to an increase in the total surface area of the silica particles. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 969–975, 2010

**Key words:** glass transition; interfaces; polystyrene; silicas

## INTRODUCTION

In recent years, polymer nanoscale composites have been used efficiently in comparison with conventional macroscale composites because of their better mechanical, thermal, and barrier properties, especially at very low filler contents.<sup>1–4</sup> It is generally agreed that the improved properties of nanocomposites are related to the modification of the structure and dynamics of the polymer due to interactions with the filler surface.<sup>5–7</sup>

A monolayer of an immobilized polymer (interfacial layer) can be produced outside each filler particle by the adsorption of polymer molecules onto the filler surface.<sup>8,9</sup> The interfacial layer thickness is determined by the state of molecular adsorption, which varies with the filler surface chemistry. However, its thickness is not more than the molecular dimensions of a polymer chain.<sup>10</sup> Because of the high surface-to-volume ratio of the nanoparticles, the adsorbed polymer fraction on the solid surface is high, so the composite properties approach those of the adsorbed polymer.<sup>11,12</sup>

Both increases and decreases in the glass-transition temperature ( $T_g$ ) have been reported for silica/polymer composites. Simple consideration of the

configurational entropy theory of the glass transition suggests that  $T_g$  should increase for polymer chains next to impermeable surfaces because of the restricted motion of polymer chains.<sup>13–17</sup> On the contrary, free volume theories of the glass transition predict that  $T_g$  will decrease because of an increase in the local free volume due to a decrease in the density of polymer chains near the filler–polymer interface.<sup>18–20</sup>

It has been suggested that the glass-transition process on heating occurs when mobile domains percolate across the specimen. In nanocomposites, the smallest interparticle spacing, which would percolate first, would dominate behavior.<sup>21,22</sup> In the case of a nonwetting interface between a polymer and a particle,  $T_g$  decreases with increasing filler volume fraction.<sup>23</sup> In contrast, increases in  $T_g$  for polymers with strong attractive filler interactions have been observed. Therefore, the processing conditions can affect the nature of the polymer–particle interface, which controls the macroscopic behavior of nanocomposite systems.<sup>23,24</sup>

At temperatures close to  $T_g$  of a polymer, an interfacial layer surrounding each filler particle appears. The thickness of this layer has been estimated to be of the order of 1–2 times the polymer radius of gyration.<sup>25,26</sup> Also, NMR measurements have confirmed the glassy nature of the polymer chains near the particle surface. This idea was recently improved by the introduction of the concept that there is a gradient of  $T_g$  around each solid particle, and this was

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quantified by Berriot and coworkers<sup>14,27</sup> for filled elastomers with both NMR and mechanical data.

In this article, we use this concept to investigate the effect of nanoparticle fillers on the shift of the glass transition of a filled polymer according to its high surface-to-volume ratio; these can create an interfacial layer better than microparticles.

## EXPERIMENTAL

### Materials

En Cuan (Taichung Hsien, Taiwan) industrial polystyrene (grade 336) with a density of 1.05 g/cm<sup>3</sup> (ISO 1183) and a melt flow index of 12 (g/10 min) was used as a matrix. Nonporous silica (Aerosil 200, 90, and OX50, Degussa Chemical, Essen, Germany) and microsilica (Iran Ferroazna) were used for the preparation of the composites under investigation. All the nanosilica particles were hydrophilic with surface areas of 200, 90, and 50 m<sup>2</sup>/g, and the average primary particle sizes were 12, 20, and 40 nm, respectively. Also, the microsilica particles were hydrophilic with a surface area of 20 m<sup>2</sup>/g, and the average primary particle size was 100 nm (0.1 μm).

### Sample preparation

A suspension (solution) method was used to prepare the composite materials.<sup>3,4,28,29</sup> Silica particles were first sonicated in toluene for 30 min, and then polystyrene was added to the suspension under magnetic stirring for 1 h. The mixture was subjected to high shear mechanical stirring at room temperature for 6 h. The resulting solution was cast onto a Teflon sheet, and this was followed by drying for 6 days and vacuum drying at 60°C for 1 day. Silica-filled polystyrene samples were molded into 1-mm-thick and 25-mm-diameter plates by hot pressing under 100 bars for 20 s at 200°C. The naming convention for defining the four contents (%) of the various silica particles used in this study is given in Table I.

### Rheological measurements

Dynamic measurements were performed with a Paar-Physica (Graz, Osterreich) UDS 200 stress-controlled rotary shear rheometer using a plate-plate geometry. The temperature sweep rheometry of all samples was performed from 90 to 160°C at 1% deformation and at a frequency of 5 Hz.

## RESULTS AND DISCUSSION

### Viscoelastic properties of the filled polystyrene

The elastic modulus of pure polystyrene exhibits a plateau at low temperatures and then a sharp decrease

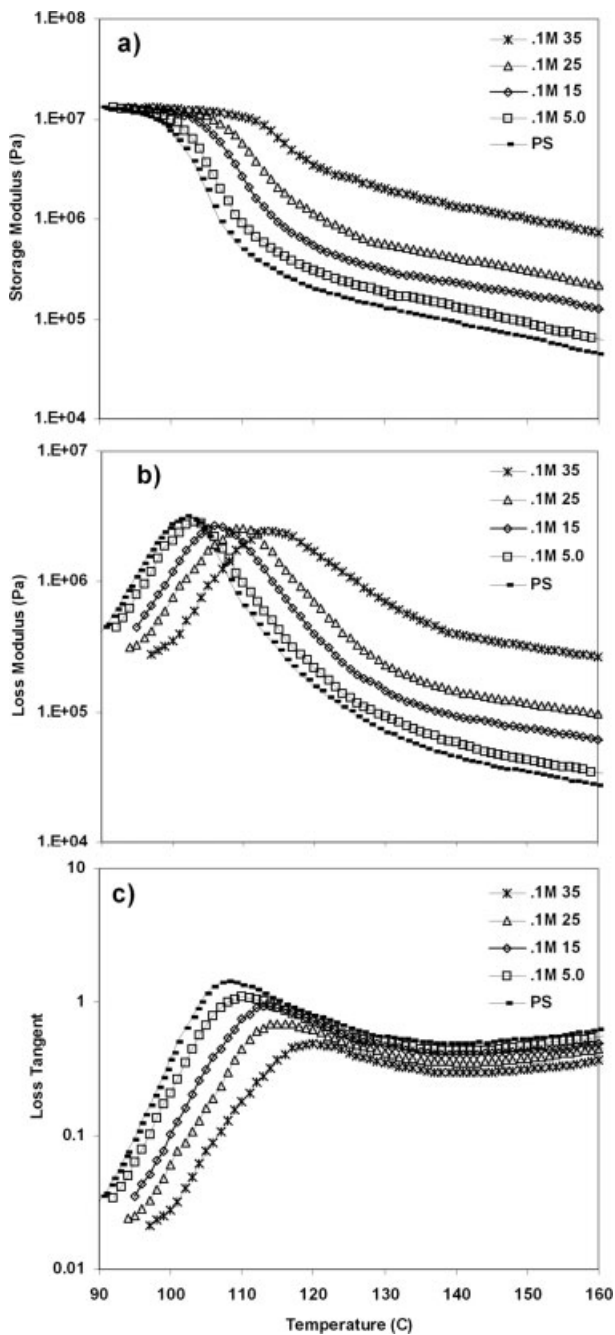
**TABLE I**  
Samples of the Silica-Filled Polystyrenes

Sample name	Filler specification		
	Particle size (nm)	Surface area (m <sup>2</sup> /g)	Volume fraction (%)
.1M 5.0	100	20	5.0
.1M 15			15
.1M 25			25
.1M 35			35
40N 2.5	40	50	2.5
40N 5.0			5.0
40N 10			10
40N 15			15
20N 1.5	20	90	1.5
20N 2.5			2.5
20N 5.0			5.0
20N 7.5			7.5
12N 0.5	12	200	0.5
12N 1.5			1.5
12N 2.5			2.5
12N 5.0			5.0

in the glass-transition domain (100–110°C), which is followed by a slight increase [Fig. 1(a)]. The results for filled polystyrene are qualitatively similar to many other data obtained for various reinforced systems.<sup>14,29</sup> The elastic modulus of microsilica-filled polystyrene demonstrates an increase in the glass-transition domain, which is broader than that of the pure polymer. The slope of the elastic modulus decreases with an increase in the filler volume fraction. Therefore, the modulus of filled polystyrene is more than the modulus of the pure polymer at higher temperatures according to the silica content. Conventionally,<sup>30</sup> filler-filler interactions, such as agglomeration and its networking, may increase the elastic modulus of highly filled polystyrene in the molten state.

The loss modulus of pure polystyrene experiences a maximum value in the glass-transition domain. Usually,  $T_g$  is determined as the temperature at which the loss modulus is maximum at the given frequency. Therefore, according to Figure 1(b),  $T_g$  of filled polystyrene changes with the filler content.  $T_g$  of pure polystyrene is around 102°C and shifts to 103, 106, 110, and 114°C with the microsilica content increasing to 5.0, 15, 25, and 35%, respectively.

It is known that the introduction of solid particles into a polymer leads to a slowdown of the motion of the polymer chains near the particle surface and causes the creation of an immobilized interfacial layer. A  $T_g$  shift is evidence that the glassy behavior of filled polymers increases in the presence of an immobilized interfacial layer around the solid particles. Accordingly, at temperatures above  $T_g$ , the reinforcement of silica-filled polystyrene is also affected by the glassy nature of the polymer segments near the particle surface. The elastic and loss moduli could



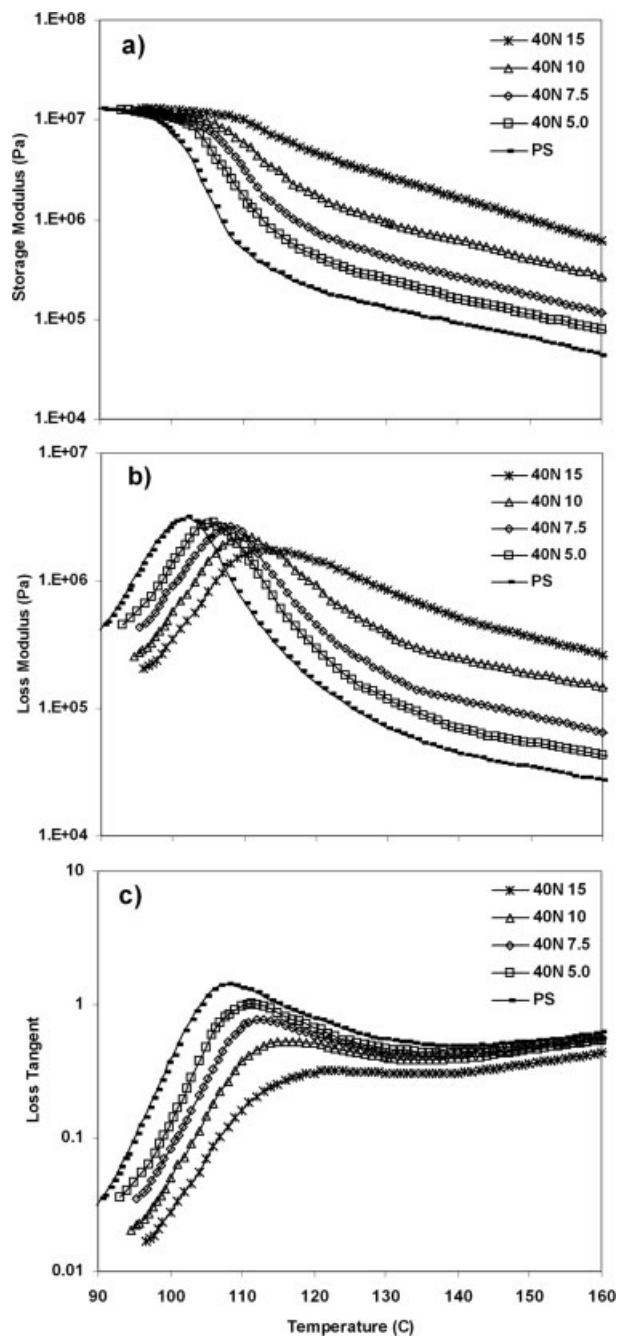
**Figure 1** Dynamic properties of the microsilica-filled polystyrene (PS) versus temperature: (a) storage modulus, (b) loss modulus, and (c) loss tangent.

be increased simultaneously with  $T_g$  growth of filled polystyrene by an enhancement of the interfacial layer volume fraction due to the presence of solid particles.

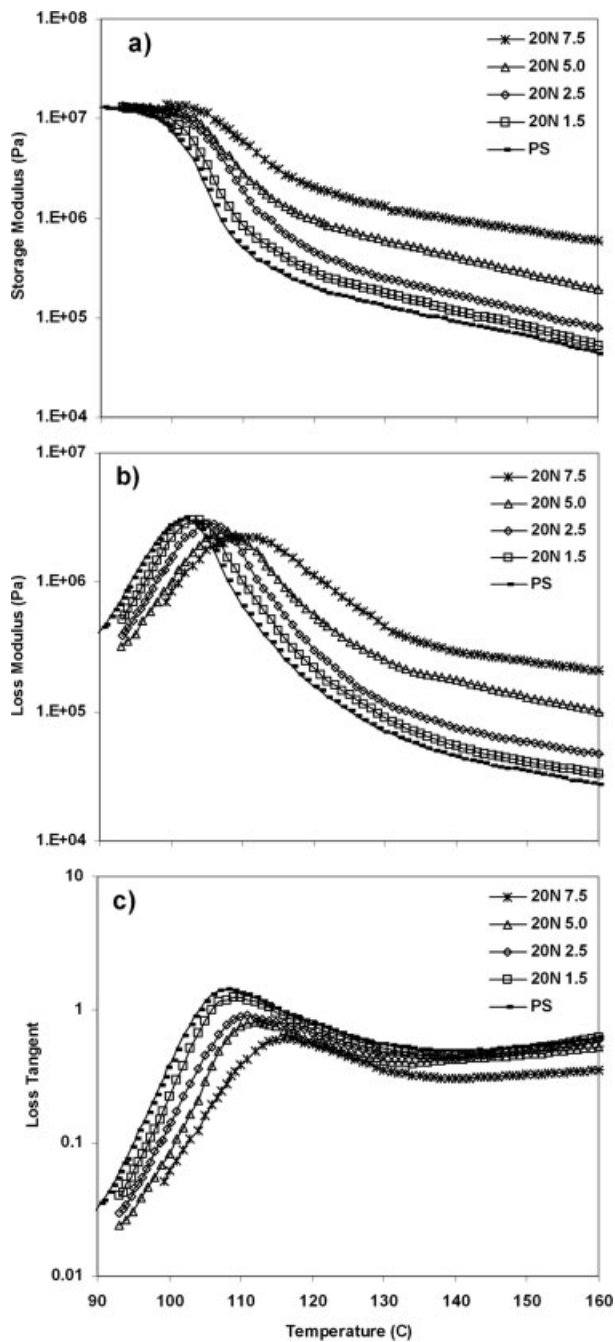
The loss tangent shown in Figure 1(c) is the ratio of the loss modulus to the elastic modulus. These results indicate that the shape and magnitude of the loss tangent are significantly affected by the volume fraction of silica particles. The loss tangent of pure polystyrene experiences a maximum value in the

glass-transition domain, and this is followed by a slight increase toward the unit ratio, which explains the liquid-like behavior. The addition of filler particles reduces the loss tangent in all temperature ranges; this is usually described as solid-like behavior and is evidence for filler-polymer interactions.

A study of the enhancement of the elastic modulus, shift of  $T_g$ , and reduction of the loss tangent leads to two proposed reinforcement mechanisms in a filled polymer with solid particles:



**Figure 2** Dynamic properties of 40-nm silica-filled polystyrene (PS) versus temperature: (a) storage modulus, (b) loss modulus, and (c) loss tangent.



**Figure 3** Dynamic properties of 20-nm silica-filled polystyrene (PS) versus temperature: (a) storage modulus, (b) loss modulus, and (c) loss tangent.

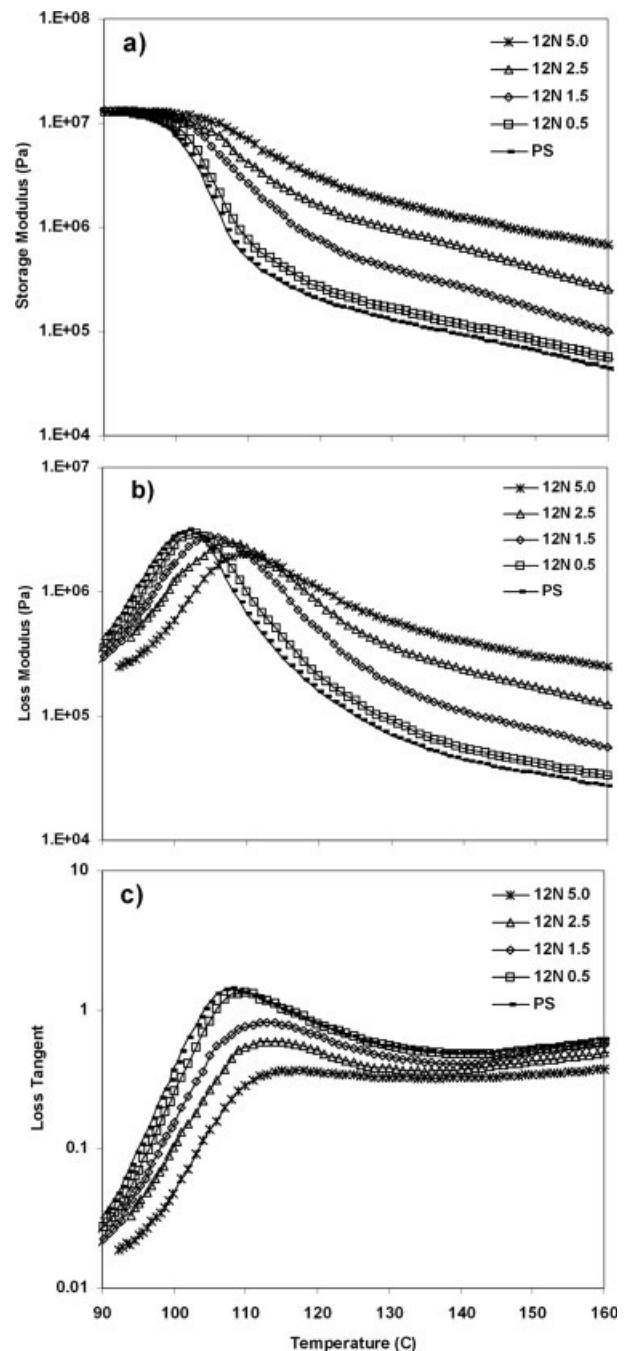
1. Filler–filler interactions such as agglomeration and solid networking.
2. A slowdown in the dynamics of the polymer chains due to the presence of solid particles and the creation of an immobilized interfacial layer.

#### Silica particle size effect

The viscoelastic properties of nanosilica-filled polystyrene are shown in Figures 2–4 with three types of

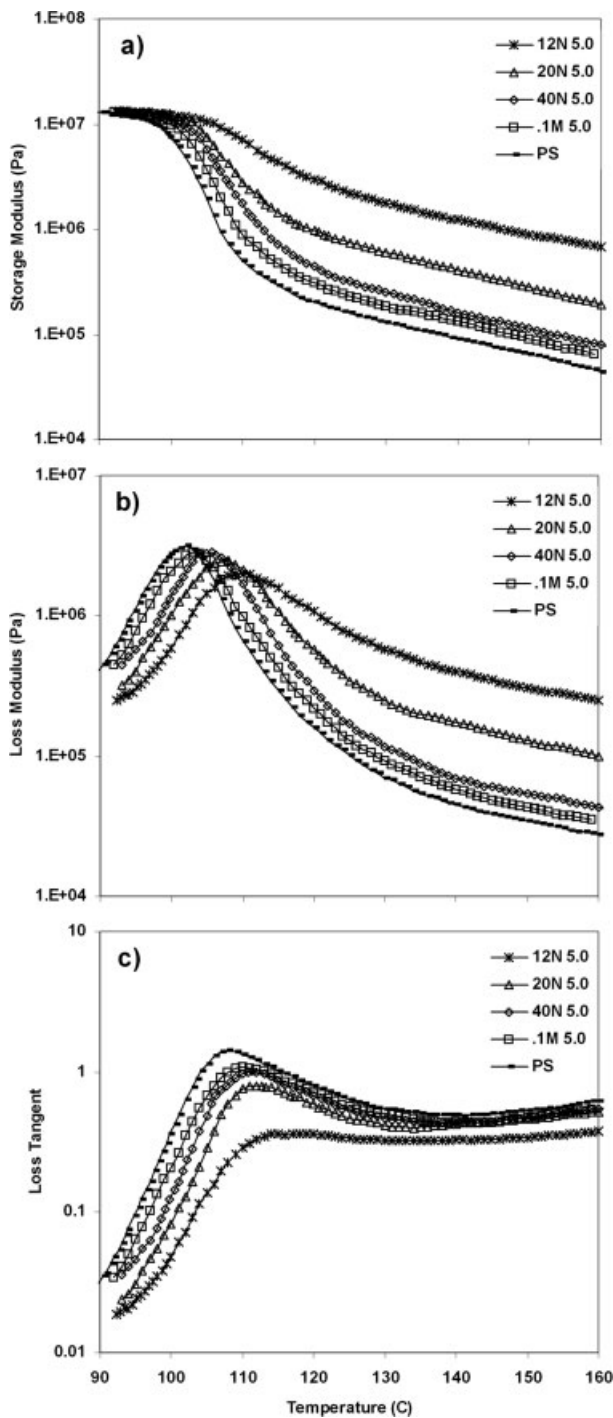
nanosilica particles (40, 20, and 12 nm). Significant reinforcement can be observed in the elastic and loss moduli for all the samples at high temperatures, and a rapid increase can be observed for the smallest silica particle (12 nm), which is related to an increase in the total surface area of the nanosilica particles.

The experimental results demonstrate that the reinforcement and  $T_g$  are strongly dependent on the filler loading for all silica particle sizes. This dependence is stronger for nanoparticles because of their



**Figure 4** Dynamic properties of 12-nm silica-filled polystyrene (PS) versus temperature: (a) storage modulus, (b) loss modulus, and (c) loss tangent.





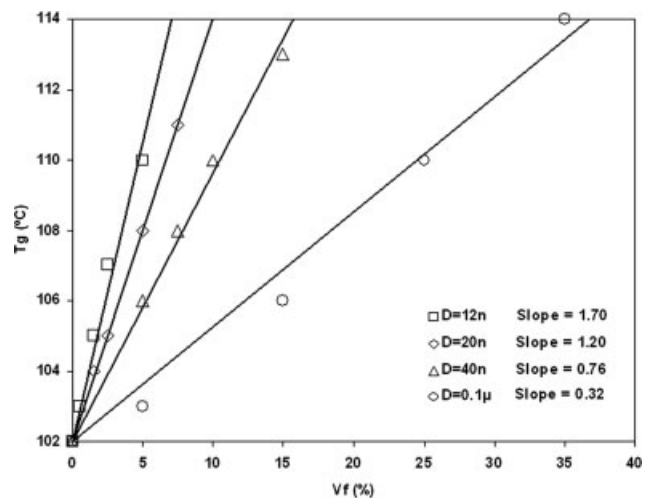
**Figure 5** Dynamic properties of different silica-filled polystyrenes (PSs) versus temperature (volume fraction = 5%): (a) storage modulus, (b) loss modulus, and (c) loss tangent.

high specific surface area, which results in an increase in the immobilized interfacial layer volume. The elastic modulus and  $T_g$  of filled polystyrene increase with the interfacial layer volume fraction, which is affected by the filler content and/or its surface-to-volume ratio (particle size). Figure 5 shows that the filler particle size plays a key role in the

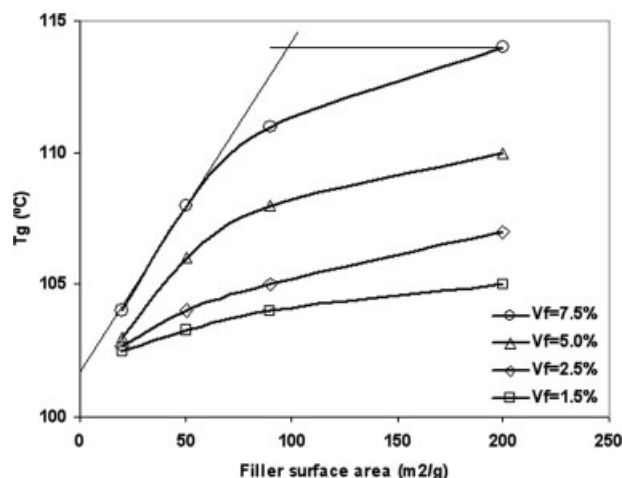
shift of  $T_g$ . As the filler particle size decreases, the filler content at which  $T_g$  increases moves to lower values; it becomes as low as 0.5 vol % for the smallest sample (12N 0.5). In this figure, the modulus increases with an increase in the filler surface area, which is caused by the filler particle size decreasing. This shows that the main source of the increase in the modulus and glass transition is the presence of the immobilized interfacial layer. This is in agreement with the observations of Sternstein and Zhu.<sup>11</sup>

The curves of the loss tangent and loss modulus of the filled polymer are broader than those of the pure polymer in the  $T_g$  region because of the presence of the solid particles in the polymer matrix. The rate of broadness of these curves is related directly to the filler concentration for all particle sizes. On the other hand, for a constant filler volume fraction, a decrease in the filler particle size has a similar effect and leads to smaller loss moduli and loss tangent peaks. This phenomenon is related to the increase in the interaction between the polymer and filler particles. We believe that the origin of this effect is the increase in the polymer-particle interface area. These results could follow the idea put forward in refs. 21, 22, and 27, which have demonstrated that in a nanocomposite, the smallest interparticle spacing dominates the thermomechanical behavior, and it is related to the filler specific surface area.

$T_g$  values of silica-filled polystyrenes (obtained from Figs. 1–4) are plotted versus the filler volume fraction in Figure 6. The slope of the  $T_g$  curve is a suitable criterion for the rate of the  $T_g$  shift, which is affected by the sizes of the particles in different silica-filled polystyrenes. This rate increases as the size of the filler particles decrease. Rheometric tests



**Figure 6**  $T_g$  of silica-filled polystyrene as a function of the filler volume fraction ( $V_f$ ) for different silica particle sizes. D, particle diameter.



**Figure 7**  $T_g$  of silica-filled polystyrene as a function of the filler surface area for different filler volume fraction ( $V_f$ ) values.

show that  $T_g$  of nanocomposites increases in the presence of filler particles. This differs from the results obtained by Torkelson et al.<sup>24</sup> This difference is mentioned by Bansal and coworkers,<sup>22,23</sup> who reported both slight increases and decreases in  $T_g$  according to the processing conditions. This difference is probably related to the fact that different methods have been used for the preparation of the nanocomposites; this is in accordance with the conclusion of Bansal and coworkers.

There is an inverse relation between the specific surface area of a filler and its initial particle size, as shown in Table I. Therefore, the effects of the specific surface area are useful for studying the effects of the filler size. To investigate the filler particle size effect,  $T_g$  has been plotted against the filler surface area for different filler volume fractions (Fig. 7).  $T_g$  of filled polystyrene increases with a particle size reduction (specific surface area growth) for all filler volume fractions.  $T_g$  increases linearly for samples with silica particles bigger than 20 nm (specific surface area < 90 m<sup>2</sup>/g). However, as the filler particle size decreases below 20 nm, the linear trend changes. This phenomenon is due to a reduction in the real surface area of the nanoparticles, in comparison with the initial specific surface area, by filler agglomeration. The  $T_g$  growth rate is proportional to the filler surface area, and it has an inverse relation with the particle size. The agglomeration of 12-nm silica particles decreases their total surface area and hence the  $T_g$  growth rate.

According to refs. 23 and 24, an increase in  $T_g$  versus the filler surface area (particle size decreasing) indicates the relationship between  $T_g$  and the filler-polymer interaction, which is a function of the interface area. It is worth noting that the interface area increases with an increase in the filler concentration

or with the use of smaller particles at a constant filler concentration. However, if filler agglomeration occurs, the active surface area decreases, so a slower  $T_g$  shift can be observed. Under ideal filler dispersion conditions,  $T_g$  of nanocomposites containing small particles can be obtained by the extrapolation of data of large-particle-containing nanocomposites. On the basis of this discussion, we can estimate the ratio of the effective filler surface area to the nominal filler surface area by a comparison of the experimental and calculated  $T_g$  values. For example, as shown in Figure 7, a  $T_g$  value of about 114°C for a nanocomposite containing a 7.5% concentration of 12-nm silica particles with a nominal surface area of 200 m<sup>2</sup>/g was experimentally obtained. However, based on a theoretical calculation, this value of  $T_g$  is related to the nanocomposites in which the effective filler surface area is 95 m<sup>2</sup>/g. Therefore, the ratio of the effective filler surface area to the nominal filler surface area for this specimen is 95/200.

## CONCLUSIONS

The effect of the silica particle size on the thermal viscoelastic behavior of filled polystyrene has been studied. It has been concluded for the studied materials that the viscoelastic  $T_g$  and dynamic modulus values are affected by the size of the filler particles. Reducing the silica particle size will increase its surface-to-volume ratio. Therefore, by a reduction of the filler particle size in a silica-filled polystyrene,  $T_g$  and the elastic modulus are increased, and the magnitude of the loss modulus and loss tangent is reduced.

The shift of  $T_g$  and the increase in the modulus due to a decrease in the filler particle size are explained not only by filler-filler interactions but also by filler-polymer interactions in the form of lower mobility of the polymer segment near the particle surface. Decreasing the filler particle size increases its surface area and the volume fraction of the immobilized interfacial layer. This interaction shifts  $T_g$  and reinforces silica-filled polystyrene at temperatures above its  $T_g$ .

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