

Evaluation of Interfacial Layer Properties in the Polystyrene/Silica Nanocomposite

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Received 18 January 2010; accepted 30 May 2010

DOI 10.1002/app.32902

Published online 26 August 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Processing conditions and final mechanical properties of polymer nanocomposites are affected by their interfacial layers behavior. However, it is impossible to determine directly the properties of these layers by dynamic rheometry tests. In this work, the interfacial layers properties are evaluated for polystyrene containing silica nanoparticles by the concept of glass-transition temperature shift. The samples were prepared via solution-mixing method and dynamic rheometry was used to determine the viscoelastic behavior of filled polymers in the melt state. This initial step showed that addition of silica particles increased the glass-transition temperature. By preference, decrease in the filler particle size lead to a drastic increase in the glass-transition temperature and

interfacial layer volume fraction due to relatively high surface area of the small filler particles. Then, in the next step, the viscoelastic properties of interfacial layer have been evaluated on the basis of the properties of neat polystyrene using temperature-frequency superposition law. For this purpose, the shift factor was calculated from the glass-transition temperature of the sample with maximum filler content. Finally, the effect of immobilized interfacial layer on the viscoelastic properties of the polymer nanocomposite samples has been estimated. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2039–2047, 2011

Key words: interfacial layer; glass-transition; silica; polystyrene; nanocomposite

INTRODUCTION

Understanding the polymer–filler interactions and the knowledge of the viscoelastic behavior of interfacial layers are crucial in the development of nanocomposites. It is generally agreed that the improved properties of nanocomposites are related to the modification of the structure and dynamic of the polymer chains in contact with the filler particles surfaces.^{1–4} When inorganic fillers are added to polymers, their particles size and volume fractions are the major factors that affect viscoelastic behavior of the nanocomposites,^{5,6} their processing conditions, and mechanical properties of the final products.^{7,8}

In nanocomposites, an immobilized polymeric layer is appeared at temperature close to glass-transition (T_g) of polymer, surrounding the filler particles.^{9–11} For many composites, it has been reported that the glass-transition temperature of interfacial layer should increase due to restricted motion of polymer chains.^{12–15} Both NMR measurements and mechanical data have confirmed the glassy nature of

the polymer chains near the particles surfaces.^{16,17} This idea has been improved by introducing the concept that there is a gradient of glass-transition temperature around solid particles.¹⁸ Also, the existence of an immobilized interfacial layer in polymer/inorganic particles nanocomposites has been shown on the basis of the heat capacity measurements at the glass transition temperature (T_g) of the polymer.¹⁹ The thickness of this immobilized layer is estimated to be on the order of 1–2 times of the polymer radius of gyration (R_g) using molecular simulation.^{20–23}

As the filler concentration increases beyond the critical volume fraction, the viscosity tends to increase until the loading level reaches the maximum volume fraction (Φ_{max}).²⁴ At this stage, filler particles wall to wall distance will be at its minimum value. It is assumed that this value is equal to an order of polymer radius of gyration. Therefore, all of the polymer chains are located in the interfacial layer and they have higher glass-transition temperature and dynamic modulus than the neat polystyrene.^{17,25}

In our previous work, the polystyrene/silica nanocomposites were prepared, and the effect of silica particle size on the thermal viscoelastic behavior was investigated.²⁶ The shift of glass-transition temperature and the modulus enhancement due to decrease in the filler particle size were explained by

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TABLE I
Conventional Coding and Viscoelastic Properties of Polystyrene/Silica Composites

Sample name	Filler volume fraction (%)	Glass transition temperature (°C) ²⁶	Storage modulus (kPa) ²⁶	Loss modulus (kPa) ²⁶
M 5.0	5.0	104	12	12
M 15	15	106	32	30
M 25	25	110	72	67
M 35	35	114	–	–
M 45	45	119	–	–
M 53	53	127	–	–
40N 5.0	5.0	104	20	21
40N 7.5	7.5	108	32	30
40N 10	10	110	–	–
40N 15	15	113	105	95
20N 1.5	1.5	104	11	13
20N 2.5	2.5	105	15	18
20N 5.0	5.0	108	41	34
20N 7.5	7.5	111	124	70
12N 0.5	0.5	103	8	11
12N 1.5	1.5	105	13	15
12N 2.5	2.5	107	26	24
12N 5.0	5.0	109	136	52

the filler–polymer interaction in the form of lower mobility of polymer segments near particles surfaces.

In this article, shift of glass-transition temperature and modulus enhancement of polystyrene nanocomposites were used to estimate the volume fraction of interfacial layer and its viscoelastic glass-transition temperature. The viscoelastic behavior of interfacial layer was also evaluated based on the properties of neat polystyrene using temperature-frequency superposition law, in which the shift factor is calculated by temperature sweep rheometry method. Finally, aside from the filler–filler interactions, the effect of immobilized interfacial layer on the viscoelastic properties of nanocomposite was studied, as well.

EXPERIMENTAL

Materials and sample preparation

Industrial polystyrene grade 336 with density 1.05 g/cm³ (ISO 1183) and melt flow index of 12 g/10 min was purchased from EN CHUAN (Taiwan, Hsien) and used as matrix. Non-porous nano-Silica Aerosil 200, 90, OX50 (supplied by Degussa, Chemical, Germany, Essen) and Micro-silica (supplied by Ferroazna, Azna, Iran) were used for the preparation of nanocomposite samples. Nano-silica particles were hydrophilic with average primary particle sizes of 12, 20, and 40 nm. Also, micro-silica particles were hydrophilic, with average primary particle sizes of 100 nm (0.1 μm). All silica particles have an individual density ~ 2.2 g/cm³.

Suspension (solutions) method was used to prepare the composite materials.^{27,28} 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 then subjected to high shear

mechanical stirring (T25 digital ultra-turrax IKA Germany) at 2000 rpm and room temperature for 6 h, to break down the silica clusters and avoid of silica particle sedimentation, during solvent evaporation. The resulting solution was cast on a teflon sheet 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. Same procedure was used in the preparation of neat polystyrene sample to keep same regime of sample preparation.

The conventional coding to define the four types of the polystyrene/silica composites was given in Table I. In this coding system, “M” or “N” refers to micro or nano particles and the left-hand and right-hand numbers indicate the particle diameter and filler volume fraction, respectively.

Characterization

A stress controlled rotary shear rheometer (Paar-Physica UDS 200, Austria, Graz) was applied in plate–plate geometry to measure the viscoelastic response of the polystyrene/silica composites. The temperature sweep rheometry was performed in temperature range 90–200°C, at 1% deformation and frequency $\omega = 5$ Hz, to obtain glass transition temperature. The frequency sweep rheometry of neat polystyrene was performed in the frequency range 0.01–500 Hz, at 1% deformation and temperature of 135, 160, and 200°C.

RESULTS AND DISCUSSION

Representation of interfacial layer

As shown in Figure 1(a), the storage modulus of neat polystyrene exhibits a plateau at low temperatures and

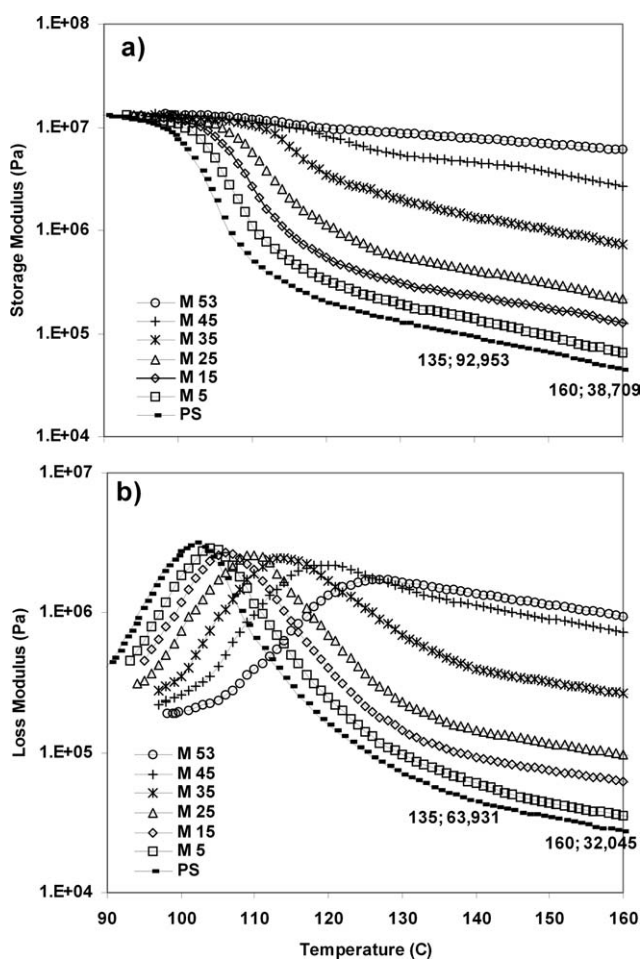


Figure 1 Shear dynamic modulus as a function of temperature for different micro-silica contents. (a) Storage modulus and (b) loss modulus.

then a sharp decrease in the glass-transition temperature domain, which is followed by a slight decrease. The storage modulus of composite demonstrates an increase in the glass-transition temperature domain which is broader than that of the neat polymer. These results are qualitatively in accordance with the result obtained by Berriot¹⁶ and Chabert.²⁷

The loss modulus of neat polystyrene experiences a maximum value in the glass-transition temperature domain [Fig. 1(b)]. Usually, a glass-transition temperature is determined by the temperature in which the loss modulus is maximal at the given frequency.²⁹ The Loss modulus of micro-silica filled polystyrene demonstrates an increase in the temperature domain above $T_{g'}$, which is broader than the neat polymer. The slope of modulus decreases by increasing the filler volume fraction (ϕ). Thus, the glass-transition temperature of the filled polystyrene sample is changed with filler content variations. Glass-transition temperature of neat polystyrene is around 102°C and shift to higher temperature with

increasing micro-silica content. The glass-transition temperatures of composites which contained four types of silica particles, i.e., 100, 40, 20, and 12 nm are presented in Table I. Filler particle size plays a key role in the shift of glass-transition temperature. The lower the size of filler particle, the lower the value of filler content at which glass-transition temperature increases.

It is known that introduction of solid particles into a polymer melt, leads to slowing down the motion of the polymer chains near the particles surfaces by making immobilized interfacial layers. Shift of glass-transition temperature is evidence to the increase of glassy behavior of composites due to the presence of immobilized interfacial layers. Accordingly, at the temperature above glass-transition temperature of matrix, reinforcement of composites is also affected by the glassy nature of the interfacial layers.

These experimental results show that the glass-transition of nanocomposites increases by the presence of the filler particle and creation of immobilized interfacial layer. These immobilized polymers join to the filler particle and create an effective particle [eq. (1)]. This model is similar to core shell system which have been used frequently in the literature.^{10,25,30}

$$\phi_{\text{eff}} = \phi + V_{\text{int}} \quad (1)$$

where, Φ_{eff} is the effective volume fraction of the fillers and Φ and V_{int} show the volume fraction of solid particles and interfacial layer, respectively.

The effective particles are spherical with a diameter of about $D + 2h$, being D and h the silica particle diameter and interfacial layer thickness, respectively. Polymer segments in the interfacial layer regions have higher glass-transition temperature and modulus than the other bulk polymer segments and cause variations in the viscoelastic properties of nanocomposites.

Since the overlap of interfacial layers in neighbor particles is neglected at low concentrations of filler, eq. (2) shows the relationship between the volume fraction of polymer matrix (V_P) with those of silica particles and interfacial layers in the effective particle model:

$$V_P + \phi + V_{\text{int}} = 1 \quad (2)$$

therefore, effective volume fraction of filler and the ratio of interfacial layer volume to filler volume (V_{int}/Φ) can be formulated by eqs. (3) and (4), respectively:

$$\frac{\phi_{\text{eff}}}{\phi} = \left(\frac{D + 2h}{D} \right)^3 \quad (3)$$

$$\frac{V_{\text{int}}}{\phi} = \left(\frac{D+2h}{D}\right)^3 - 1 \quad (4)$$

From the latter equation, the ratio of interfacial layer volume to volume of filler is dependent on the interfacial layer thickness and filler particle size. Zhang et al.³ explained these relations by the ratio of filler surface to its volume. They estimated that the effective filler volume fraction is about 6 times as large as the real nano-particle volume fraction.

Evaluation of interfacial layer properties

At maximum filler concentration, the interfacial layers overlap each others and the effective particles have a diameter about $D + h$. Thus, the maximum filler concentration of solid particles is calculated according to eq. (5) as a function of maximum filler concentration of the effective particles ($\phi_{\text{max}}^{\text{eff}}$):

$$\phi_{\text{max}} = \phi_{\text{max}}^{\text{eff}} \left(\frac{D}{D+h}\right)^3 \quad (5)$$

This equation is similar to what has been obtained by Privalko et al.³¹ In monodispersed hard sphere systems, the maximum value of filler concentration depends on several parameters such as type of packing and geometric arrangement of the spheres, although it is independent on the particle diameter. The maximum value of filler concentration has been investigated by several researchers,^{24,32–34} and the value is commonly near to 64 vol % which is random close packing value of maximum filler concentration.

Since, filler concentration is at its maximum amount, filler particles wall to wall distance (S) will be equal to interfacial layer thickness (h), and all of polymer chains will be located in the interfacial layer (Fig. 2). Therefore these polymer chains will have a more dynamic modulus than that of the neat polystyrene. As a conclusion, the effective particles will be similar to monodispersed hard sphere, and the maximum effective filler concentration will be estimated about 0.64. Finally, the maximum filler concentration of silica particles as a function of interfacial layer thickness is calculated by eq. (6):

$$\phi_{\text{max}} = 0.64 \left(\frac{D}{D+h}\right)^3 \quad (6)$$

As shown in Figure 2, interfacial layer thickness is equal to the wall to wall distance of silica particles at maximum filler concentration. The volume of interfacial layer increases due to the enlargement of the filler surface area, which is caused by decrease of the filler particle size. Thus, the volume ratio of

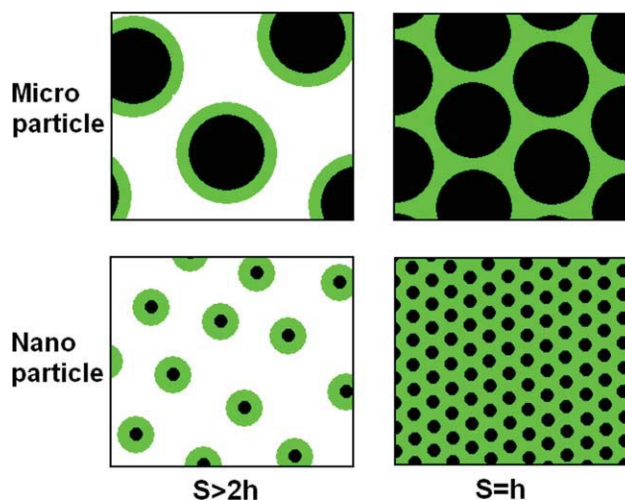


Figure 2 Schematic of interfacial layer for two different silica particle sizes at maximum filler content ($S = h$), compared to that of low filler content ($S > 2h$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interfacial layer to silica particle increases by decreasing the filler particle size.

In the filled polymer systems, the filler particle wall to wall distance decreases by increasing filler concentration and reach to a minimum value at maximum filler concentration. This minimum wall to wall distance has a value in the order of polymer radius of gyration. Therefore, in these cases, the maximum volume fraction of nano-particles is smaller than the maximum volume fraction of micro-particles. It means that the maximum filler concentration reduces with decrease of the filler particle size [according to eq. (6)], which is caused by increase in the effective particle volume fraction.

The maximum filler loading of micro-silica/polystyrene composite is about 53 vol % of micro-silica particles, because higher filler loading does not lead to reasonable consistency. This volume fraction represents the maximum filler concentration of micro-silica in polystyrene. In this case, silica particles wall to wall distances are smaller than $2h$, so all of polymer chains are subjected to the interfacial layer and behave similar to the immobilized chains. Thus, it can be assumed that the T_g of interfacial layer is equal to the T_g of composite containing maximum filler concentration:

$$T_{g_{\text{int}}} = T_{g(\phi=\phi_{\text{max}})} \quad (7)$$

As can be seen in Table I, the glass-transition temperature of composite containing 53 vol % micro silica is about 127°C. This temperature is called $T_{g_{\text{int}}}$ which is attributed to the interfacial layer glass-transition temperature.

According to mixing rule, the glass-transition temperature of composites is an average of the neat

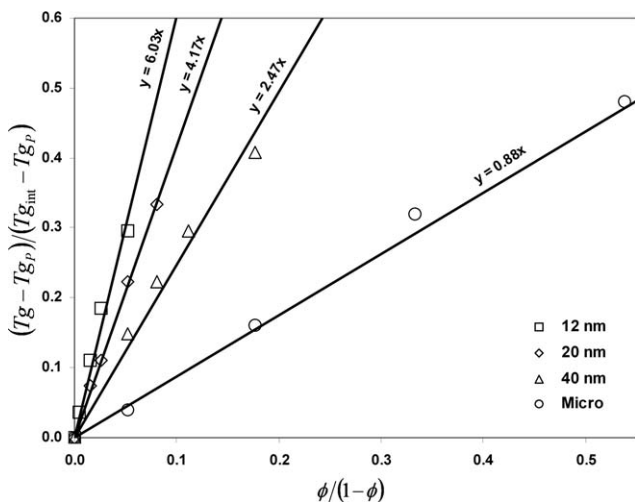


Figure 3 Reduced T_g of polystyrene/silica composite as a function of relative filler volume fraction for different silica particle sizes.

polystyrene glass-transition (T_{gp}) and the interfacial layer glass-transition (T_{gint}):

$$T_g = \frac{V_p * T_{gp} + V_{int} * T_{gint}}{V_p + V_{int}} \quad (8)$$

Rearrangement of this equation can propose the eq. (9) as the practical formulation for the volume fraction of interfacial layer, based on the shift of glass-transition temperature:

$$\frac{T_g - T_{gp}}{T_{gint} - T_{gp}} = \frac{V_{int}}{\phi} \cdot \frac{\phi}{1 - \phi} \quad (9)$$

In Figure 3, the left hand side of eq. (9) is plotted as a function of $\Phi/(1 - \Phi)$ for four different silica-containing composites. The slope of these curves gives the ratio of interfacial layer volume to filler volume (V_{int}/Φ) for several silica particle sizes.

It is worth mentioning that, V_{int} consists of the volumes of the polymer chains at the interfacial layers around the filler particles and the volume of polymer chains trapped among them. Then, an equivalent interfacial thickness relates to this V_{int} is proposed as follows, as a practical formulation according to eq. (4):

$$h = \frac{D}{2} \left[\sqrt[3]{\left(\frac{V_{int}}{\phi} + 1\right)} - 1 \right] \quad (10)$$

By using eqs. (9) and (10), the relative volume fraction and thickness of interfacial layers are plotted as a function of the filler particle size in Figure 4. Drastic increase in the volume fraction of interfacial layer is referred to relatively high surface area of nano-particle. The small size of the nano-particles

generates a very large surface area to be coated by the polymer chains which causes a huge immobilized interfacial layer. This high surface area compared to that of micro-particles, means that at the same filler concentration, the interfacial layer volume in nanocomposites is larger than the one in microcomposites.

As can be seen in Figure 4, thickness of interfacial layer is decreased by decreasing the filler particle sizes and it is around 5 nm for the smallest particles, which is similar to the results obtained by other researchers.^{3,18,21,23} However, the value of the interfacial layer thickness depends on each sample and varies with polymer molecular weight, filler surface properties, particle size, dispersion state, and processing conditions, as well.

Berriot et al.¹⁷ examined the properties of the polymer near the interface with the filler particles and found that the dynamic modulus of polymer matrix depends on the distance between the position of polymer chain and the nearest interface. A shift in glass transition will lead to spatial variations of the elastic modulus. Thus, at any temperature above the glass transition of interfacial layer, the elastic modulus of the interfacial layer G_{int} , will depend on the shift of glass-transition temperature (ΔT_g), as expressed by:

$$G_{int}(T, \omega) = G_p(T - \Delta T_g, \omega) \quad (11)$$

By using Table I and eq. (7), the shift of glass-transition temperature from that of neat polystyrene to that of interfacial layer is about 25°C. Thus, the eq. (11) could be rewritten for storage and loss modulus of interfacial layer, at any temperature above the glass transition of interfacial layer, based on the neat polystyrene properties at lower temperature, for example at $T_1 = 160^\circ\text{C}$, it will be:

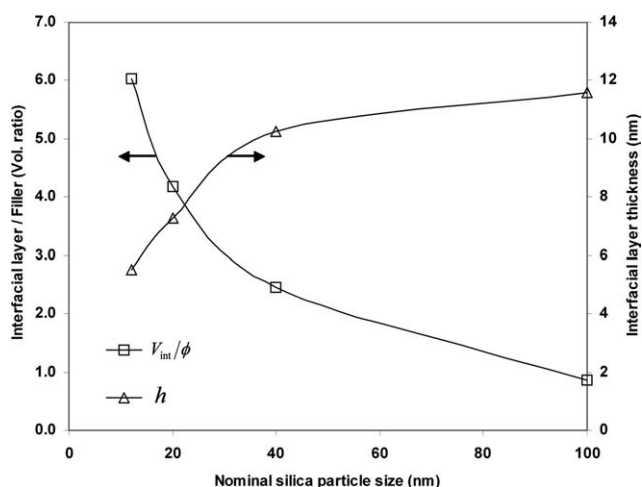


Figure 4 The relative volume fraction and thickness of interfacial layer versus silica particle size.

$$\begin{cases} G'_{\text{int}}(T_1 = 160^\circ\text{C}, \omega_1 = 5\text{Hz}) = G'_p(T_2 = 135^\circ\text{C}, \omega_1 = 5\text{Hz}) \\ G''_{\text{int}}(T_1 = 160^\circ\text{C}, \omega_1 = 5\text{Hz}) = G''_p(T_2 = 135^\circ\text{C}, \omega_1 = 5\text{Hz}) \end{cases} \quad (12)$$

From Figure 1, the storage and loss modulus of neat polystyrene at $T_2 = 135^\circ\text{C}$ are about 93 and 64 kPa, respectively. These values are related to the storage and loss modulus of interfacial layer at $T_1 = 160^\circ\text{C}$ [eq. (12)]. On the other hand, in Figure 5, the experimental data on storage and loss modulus of neat polystyrene were plotted as a function of the fre-

quency for two temperatures, 135 and 160°C . Figure 5 demonstrate that the modulus of neat polystyrene at $T = 135^\circ\text{C}$ and $\omega = 5\text{ Hz}$ is equal to its modulus at $T = 160^\circ\text{C}$ and $\omega = 18\text{ Hz}$. Substitution of these data in eq. (12) gives the modulus of interfacial layer at $\omega = 5\text{ Hz}$, which is equal to modulus of neat polystyrene at $\omega = 18\text{ Hz}$ and same temperature ($T_1 = 160^\circ\text{C}$):

$$\begin{cases} G'_{\text{int}}(T_1 = 160^\circ\text{C}, \omega_1 = 5\text{Hz}) = G'_p(T_1 = 160^\circ\text{C}, \omega_2 = 18\text{Hz}) \\ G''_{\text{int}}(T_1 = 160^\circ\text{C}, \omega_1 = 5\text{Hz}) = G''_p(T_1 = 160^\circ\text{C}, \omega_2 = 18\text{Hz}) \end{cases} \quad (13)$$

By using temperature-frequency superposition law,³⁵ the temperature-frequency shift factor (a_T) is calculated from the ratio of the two frequencies in the eqs. (12) and (13):

$$a_T = \frac{\omega_2}{\omega_1} = \frac{18}{5} = 3.6 \quad (14)$$

Finally, the storage and loss modulus of interfacial layer can be generally calculated by using temperature-frequency shift factor according eq. (15):

$$\begin{cases} G'_{\text{int}}(T, \omega) = G'_p(T, a_T\omega) \\ G''_{\text{int}}(T, \omega) = G''_p(T, a_T\omega) \end{cases} \quad (15)$$

Under our experimental conditions, at any constant temperature more than 127°C and less than polymer degradation temperature (for example 200°C), storage and loss modulus of interfacial layer is obtained by eq. (16):

$$\begin{cases} G'_{\text{int}}(T = 200, \omega) = G'_p(T = 200, 3.6\omega) \\ G''_{\text{int}}(T = 200, \omega) = G''_p(T = 200, 3.6\omega) \end{cases} \quad (16)$$

From above discussion, one can conclude that the viscoelastic properties of interfacial layer could be obtained based on those of neat polystyrene using temperature-frequency superposition law. To achieve this, a shift factor can be calculated from variations of glass-transition temperature, using eqs. (12)–(14). Following this, the eq. (16) is used to estimate the effect of interfacial layer on the viscoelastic properties of polystyrene/silica composites.

Estimation of interfacial layer effect

The effect of the immobilized interfacial layer on the viscoelastic properties of polystyrene/silica compo-

sites can be estimated. In this approach, the contribution of hydrodynamic and filler–filler interactions, such as agglomeration and its networking is

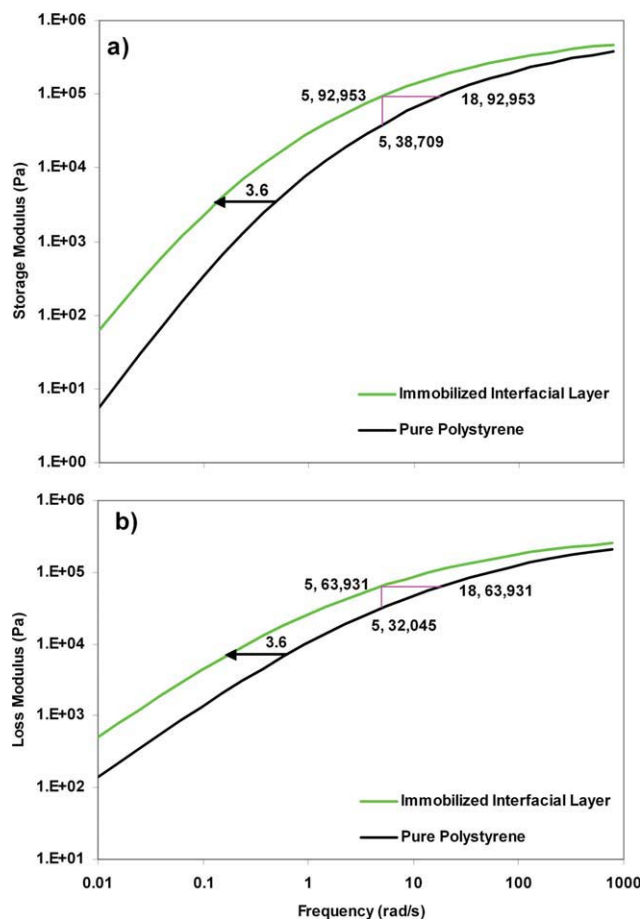


Figure 5 Frequency response of interfacial layer in the polystyrene/silica composites at $T = 160^\circ\text{C}$. (a) Storage modulus and (b) loss modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

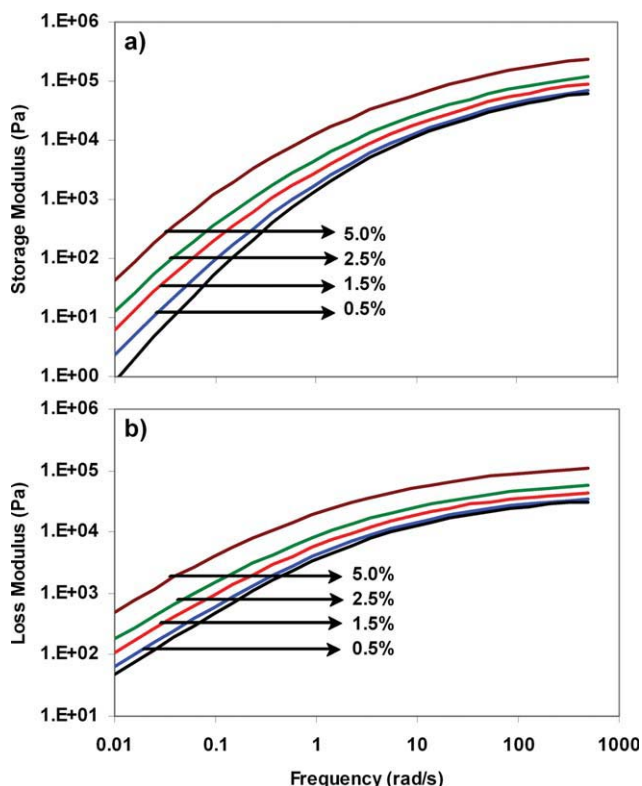


Figure 6 Shear dynamic modulus of nanofilled polymer systems at constant filler particle size (12 nm) and different filler volume fractions at $T = 200^\circ\text{C}$. (a) Storage modulus and (b) loss modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

skipped. Thus, the observed increase in dynamic linear response with the decrease of filler particle size is due to the increase of the interfacial layer volume fraction. It is caused by filler–polymer interaction in the form of lower mobility of the polymer segment near the particle surface. Increase in the composite modulus, represents the longest relaxation time of the polymer chain in the interfacial layer.

With these assumptions, the dynamic modulus of composites can be calculated on the basis of the modulus of neat polymer and interfacial layer using the mixing rule:

$$\begin{cases} G' = (1 - \phi_{\text{eff}})G'_p(T, \omega) + \phi_{\text{eff}}G'_{\text{int}}(T, \omega) \\ G'' = (1 - \phi_{\text{eff}})G''_p(T, \omega) + \phi_{\text{eff}}G''_{\text{int}}(T, \omega) \end{cases} \quad (17)$$

In eq. (17), effective filler volume fraction can be calculated from eq. (3) and dynamic modulus of neat polymer and interfacial layer were obtained from Figure 5. The storage and loss modulus in a frequency sweep for various nano filler concentration was plotted in Figure 6, using eq. (17). In the absence of agglomeration and networking, the typical slopes of neat polystyrene at low frequencies for storage and loss modulus are 2 and 1, respectively.

When the filler–filler interactions are neglected, these slopes are constant for composites and the effect of interfacial layer is presented by uniform enhances in the storage and loss modulus values.

Figure 7 shows the variation of the storage and loss modulus in a frequency sweep at 5 vol % for different filler particle sizes. Theoretical evaluations showed that the dynamic modulus of nanocomposites increases with the decrease of the filler particle size (by increasing the particles surface area and interfacial layer volume fraction).

In Figure 7, the storage and loss modulus were also compared and showed that increment is more significant in storage modulus. This is attributed to lower mobility and glassy nature of polymer chain in the interfacial layer. This phenomenon causes the composite to behave as a solid like material. It is known that the solid-like plateau at higher frequencies is due to the fact that no relaxation mode exists any longer than the relaxation time of the neat polymer chain. In the presence of nano particle fillers, the plateau region is stretched to lower frequencies. This observation indicates a longer relaxation time for the polymer chain in the composite compared to neat polystyrene. Therefore, when the filler particles

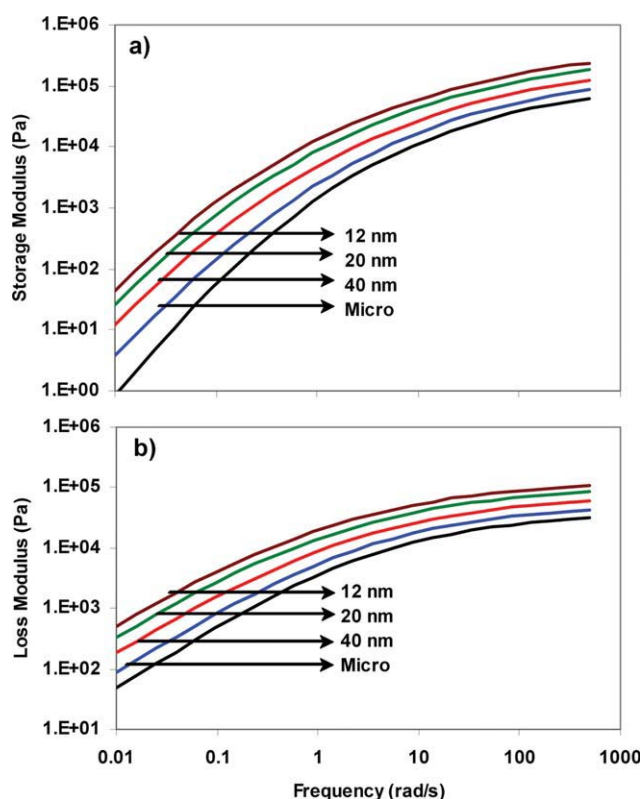


Figure 7 Shear dynamic modulus of nanofilled polymer systems at constant filler volume fraction (5%) and different particle sizes at $T = 200^\circ\text{C}$. (a) Storage modulus and (b) loss modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

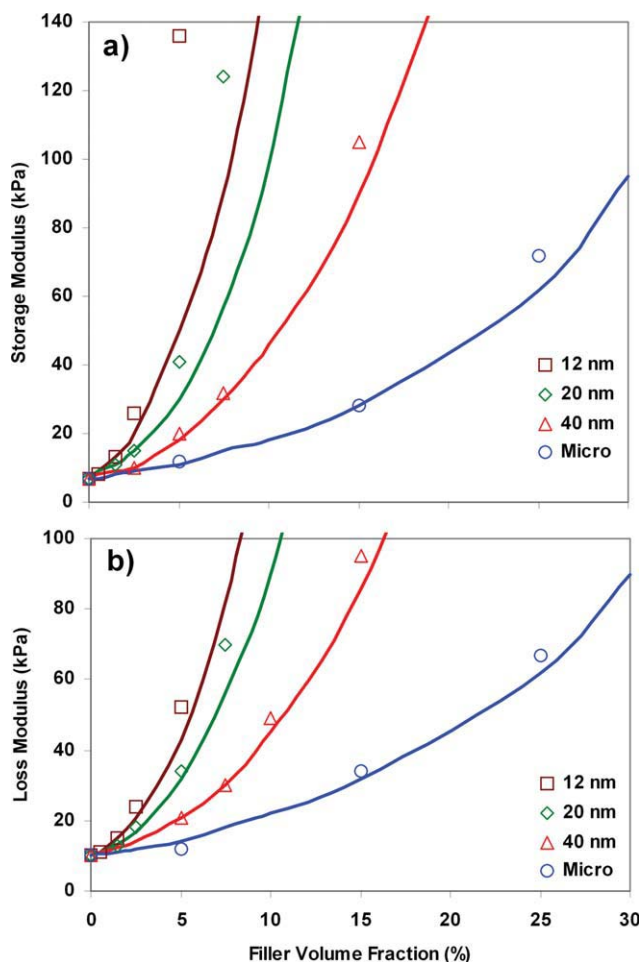


Figure 8 Experimentally measured modulus of polystyrene/silica nanocomposites at $T = 200^{\circ}\text{C}$ (dots) and theoretical predictions based on the immobilized interfacial layer effects (continuous lines). (a) Storage modulus and (b) loss modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

size decreases, the stress relaxation is affected by the presence of huge immobilized interfacial layer.

The comparison between the experimental data of polystyrene/silica nanocomposites having different silica particles and dynamic modulus prediction by interfacial layer model [eq. (17)] is presented in Figure 8. As can be seen from Figure 8, the predicted moduli by interfacial layer model are lower than the experimental data. This could be attributed to the contribution of filler–filler interaction which has been neglected. When the filler volume fraction is low, in the absence of agglomeration and networking, the typical slopes of modulus curves can be obtained for all samples type, which is comparable to conventional composites theory. However the modulus increment at higher filler volume fraction is stronger which is due to the fact that the interfacial layers on neighboring fillers were overlapped one another.

Results showed that the dynamic modulus of nanocomposites increase simultaneously with the

increase of the glass-transition temperature. These imply that the main source of increase in modulus and glass transition is the presence of the immobilized interfacial layer and the secondary networking which takes place through direct short-range interactions through overlapping of interfacial layers on neighboring fillers. This is in agreement with the observations of Sternstein and Zhu.⁵ The secondary network forms at lower concentration of nano-silica in comparison with the micro-silica, in contact to the higher interfacial layer volume fraction which is caused by higher filler surface to volume ratio.

On the linear viscoelastic properties, the mechanism of reinforcement could be based on two conceptual aspects. The concept of filler networking that yields a good interpretation of the Payne effect for filled elastomers that was reported by Cassagnau.¹ And the concept of the temperature dependence of the modulus, as consequences of the variation of polymer–filler interaction.⁵ It was suggested a common mechanism which was rooted in the macromolecular natures of the polymer matrices, as explained in our previous glass transition study.²⁶ A more complete viscoelastic model containing both filler–filler and filler–polymer interactions can be offered by taking in account of two mentioned mechanisms.

CONCLUSIONS

It was shown experimentally that the glass-transition temperature of polystyrene/silica composites is affected by the presence of fillers and their particles size. Decrease of particle size increases the surface to volume ratio of the filler and causes the raise of the glass-transition shift. It can be concluded for the studied materials that the glass-transition temperature increases simultaneously with the viscoelastic properties due to the decrease in the filler particles size. It was explained by the filler–polymer interaction in the form of lower mobility of polymer segment near the particle surface. It was also shown that the small filler particles increase the volume fraction of immobilized interfacial layer, which increases the overall glass-transition temperature. This ability is due to high surface to volume ratio of nano fillers, which forms a huge immobilized interfacial layer. Based on the experimental results, the volume fraction, glass-transition temperature, and the temperature-frequency shift factor of interfacial layer were evaluated using concept of glass-transition shift. Then, the viscoelastic properties of interfacial layer were evaluated on the basis of the properties of neat polystyrene using temperature-frequency Superposition law. Finally, the effect of immobilized interfacial layer on the viscoelastic behavior of nanocomposites was estimated. It was demonstrated that the immobilized interfacial layer can enhance

uniformly the increase in storage and loss modulus in the absence of filler–filler interactions.

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