

Study of Viscoelastic Properties of Nanocomposites of SiO₂-Acrylonitrile-Butadiene-Styrene

Ali Haghtalab, Sedighe Rahimi

Department of Chemical Engineering, Tarbiat Modares University, Tehran 14115-143, Iran

Correspondence to: A. Haghtalab (E-mail: haghtala@modares.ac.ir)

ABSTRACT: Nanocomposites of acrylonitrile-butadiene-styrene (ABS) and nanosilica with different nanoparticle sizes and various loadings are prepared. Rheological experiments such as frequency sweep, strain sweep, and rotational test are performed to investigate the influence of nanoparticle loading and size on the viscoelastic properties of the nanocomposites. The results show that nanocomposites with higher filler loading and smaller particle size have both higher storage and loss moduli. Moreover, the results indicate that the storage modulus is more sensitive than loss modulus to filler loading and nanoparticle size. The smaller nanoparticles and higher filler loadings lead to the enhancement of nanoparticle surface area so that the viscoelastic properties are intensified through increase of polymer chain adsorption on nanoparticle, and creation of a network structure in the nanocomposites. The network structure causes changes to the rheological behavior of the nanocomposite such as solid-like behavior in the low-frequency region and reduction of the Newtonian region. The scanning electron microscopy micrographs revealed that the particle aggregates increase with particle size reduction and increasing nanoparticle content. We also used a nonlinear optimization to obtain the parameters of a multimode Maxwell model for low nanofiller content ABS/SiO₂ nanocomposites and found the relaxation times of the polymer chains increased with increasing nanoparticle content. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: nanocomposite; silica; acrylonitrile-butadiene-styrene; rheology; generalized Maxwell model

Received 24 January 2011; accepted 9 May 2012; published online

DOI: 10.1002/app.38041

INTRODUCTION

Nanoparticles have been recently used as reinforcing agents in different kinds of polymer composites, to improve mechanical properties of polymeric materials. Fumed silica has a large surface area, used as a filler and will enhance interparticle interactions, which has a major impact on the rheological and reinforcement properties of nanocomposites.¹ Acrylonitrile-butadiene-styrene (ABS) is a common thermoplastic used to make light, rigid molded products such as piping, musical instruments, golf club heads, automotive body parts, wheel covers, enclosures, protective headgear, etc.² The rheological properties of nanocomposites are necessary for the process design of plastics; moreover, rheology is a tool used to assess the state of dispersion of nanocomposites in the melt state.¹ Nanoparticle's tendency to associate into extended structures can dominate the rheological, viscoelastic, and mechanical properties of the nanocomposite and hence thermodynamic factors that affect nanoparticle dispersion can be crucially important.³

The effects of nanoparticles on the different viscoelastic properties of nanocomposites have been investigated so that the various changes in mechanical behavior of polymer composite

could be observed. Several authors investigated that particle size is an effective parameter in viscoelastic properties of composite polymer melts.^{4–9} For example, Jianga et al.⁷ studied the composites of acrylonitrile-butadiene-styrene (ABS) reinforced with micron and nano-sized precipitated calcium carbonate particles. They found that composites with micron size particles have higher modulus but lower tensile and impact strength than neat ABS, whereas nano-sized precipitated calcium carbonate enhanced the moduli of ABS and maintained or even increased its impact strength within a certain nanoparticle loading range. Osman⁸ also investigated the effect of the size of calcium carbonate particles on high-density polyethylene composites. They concluded that the larger contact area of nanoparticles relative to that of microparticles leads to propagation of more and stronger filler clusters in the composites. Haghtalab and Marzban⁹ investigated the effect of nanosilica particles on the rheological properties of polypropylene with respect to the influence of particle loading and size. The surface-treated nanoparticles showed better dispersion in the polymer so that a reduction of dynamic moduli was observed by changing the particle's surface energy.^{4,8,10} The surface treatment of nanosilica particles by hexadecyltrimethoxysilane with production of superhydrophobic

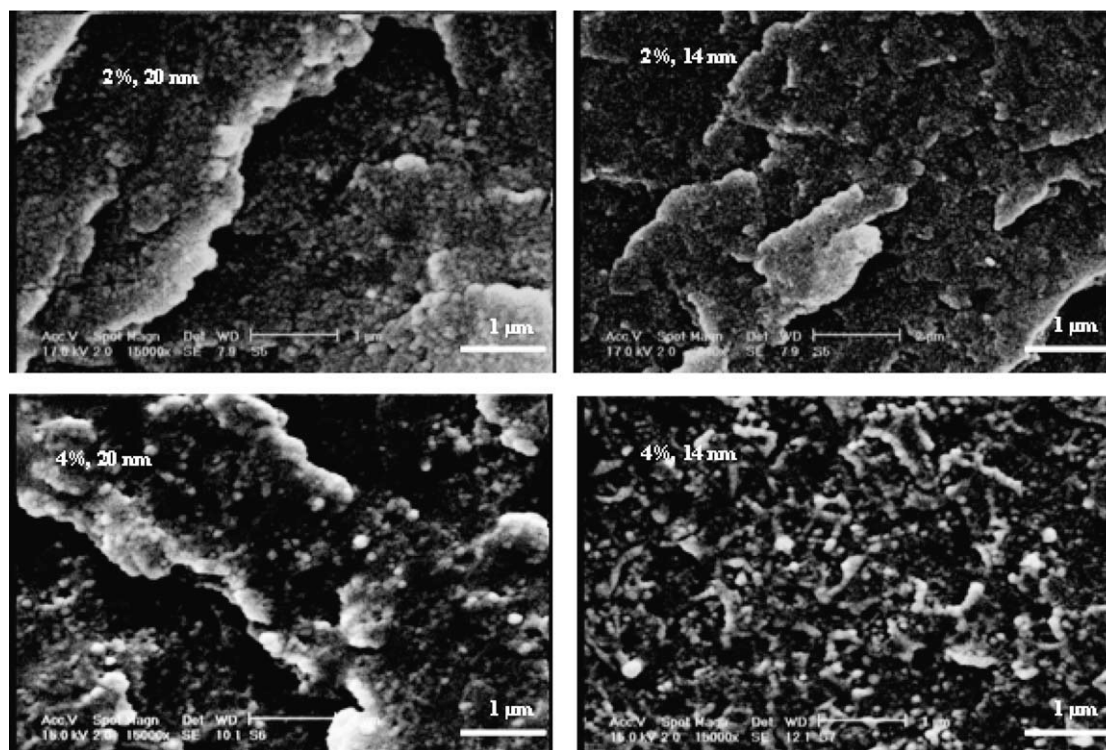


Figure 1. SEM micrographs of ABS/SiO₂ nanocomposites with different nanoparticles weight percent content.

nanosilica lead to uniform dispersion of particles in polydimethylsiloxane (PDMS) and better thermal stability than untreated nanosilica-filled PDMS.¹⁰ Suetsugu and White⁴ investigated the effect of both of the particle size and surface coating of CaCO₃ on the rheological properties of suspended molten polystyrene and concluded that surface treatment is most effective for the smallest particle size, reducing particle agglomeration. Clement et al.¹¹ observed that the amplitude of the Payne effect is reduced by the treatment of the silica particles. Payne effect is a rheological observation that has been studied by the several authors.^{11–14} Cassagnau¹³ studied viscoelastic properties of nonporous silica dispersed in ethylene vinyl acetate copolymer, from diluted solution to molten polymer, and concluded that depending on silica concentration and deformation amplitude, nonlinearity such as Payne effect is affected by both chain disentanglements and filler network breakdown. In a review article, Cassagnau¹ also concluded that particle–particle interactions are the dominant mechanism responsible for changes in viscoelastic properties in fumed silica nanocomposites. He believes that the filler network breakdown is adequate for describing the strain dependence of dynamic mechanical properties of composites.¹⁴ The solid-like behavior nonlinearity has been found in many nanocomposites at high filler loading in the low-frequency region^{7–9,15,16} and in most of them, a network formation by the particles is considered the cause for such behavior.

The study of dynamic–mechanical properties of nanocomposites is very useful in explaining how the behavior of polymeric chains is influenced by nanoparticles. At low filler concentration and before the onset of solid-like behavior, the relaxation time spectrum can show the effect of nanoparticles on the polymer

chains dynamics. In this case, the polymer chain adsorption on particles is the dominant mechanism for changes in viscoelastic properties of nanocomposites. The small-amplitude oscillatory shear experiments have been used to determine the parameters in a multimode Maxwell model so that the relaxation spectrum could be obtained, which is an important tool for studying the behavior of viscoelastic properties of polymeric materials.¹⁷ The discrete relaxation spectrum has been calculated for different polymeric systems using the multimode Maxwell model.^{17–19} These parameters for polyamide-6 (PA6) and a low concentrated clay nanocomposite of PA6 were determined from linear dynamic experiments and an extra Maxwell mode was observed for the nanocomposite.¹⁹

The objectives of the present research are to characterize the effect of content and the size of nano-SiO₂ particles on the various rheological properties of the ABS/SiO₂ nanocomposites. Additionally, we will see how nanoparticles influence the Maxwell model parameters of the composites with low concentrations of nanoparticles.

EXPERIMENTAL

Materials

ABS 50, a copolymer of acrylonitrile, butadiene, and styrene was obtained from Golpayegan Petrochemical (Iran). This general purpose grade ABS has a melt flow index (ISO 1133) of 34 g/10 min (220°C/10 kg) and specific gravity of 1.04 (23°C). Four types of hydrophilic fumed silica with specific surface areas 200, 150, 90, and 50 m²/g were from Degussa (Germany) The average particle diameters were 12, 14, 20, and 40 nm, respectively.

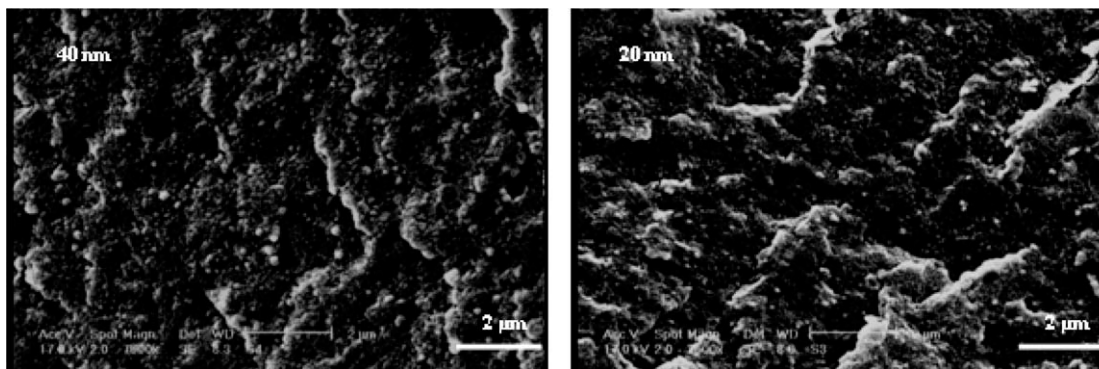


Figure 2. SEM micrographs of the ABS/SiO₂ nanocomposites with 40 and 20-nm particle sizes at 8 wt % loading.

Sample Preparation

Nanocomposites of ABS/SiO₂ were prepared by mechanical melt mixing method in an internal mixer (Berander, 50EHT). The composites were prepared with different weight fractions of nanoparticles, 2, 4, 8, and 16 wt %, to investigate the behavior of nanocomposites at different loadings.

Before the preparation of samples, materials were oven dried at 80°C for 24 h. ABS and nanoparticles were mixed in an internal mixer at a speed of 60 rpm and 170°C, for 10 min.

Testing

Fracture surfaces of samples broken after immersion in liquid nitrogen were gold coated, and a Philips electron microscope was used to study the nanosilica distribution in the nanocomposites. The rheological properties were measured using a strain-controlled rheometer (UDS200) with parallel plate geometry, 25 mm diameter, and 1 mm gap, at 200°C. Strain sweep, frequency sweep, and steady shear tests were carried out to determine the dynamic properties and the linear viscoelastic region of nanocomposites.

The strain amplitude sweep oscillation experiments were carried out at γ from 0.05 to 1000%, and a fixed angular frequency of $\omega = 1$ rad/s. The frequency sweep tests were performed at ω from 0.05 to 500 rad/s and at fixed $\gamma = 1\%$. Finally, the rotational tests, including steady shear tests, were carried out at γ from 0.001 to 10.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

Figure 1 shows the scanning electron microscopy (SEM) results of the ABS/SiO₂ nanocomposites at different loadings of nanosilica particles where the white dots represent nanoparticle aggregates which are in the nanocomposites with 2 wt % of filler. Increasing filler loading, the amount of clusters grows. The cluster sizes are also found to be different in nanocomposites with different nanofiller loadings and nanoparticle sizes.

Figure 2 shows nanoparticle clusters in composites with 8 wt % of 40- and 20-nm silica. The reduction of nanosilica size on nanocomposites containing 8 wt % has a similar effect to the increase of nanosilica loading on nanocomposites. With the reduction of nanosilica size, the amount of clusters grows, because the interparticle interaction energy increases, and hence more and the stronger clusters are produced in the nanocomposite.

Rheological Properties

By increasing filler content, the distances between particles are reduced and the higher interparticle interactions induced lead to the production of a filler network structure in the

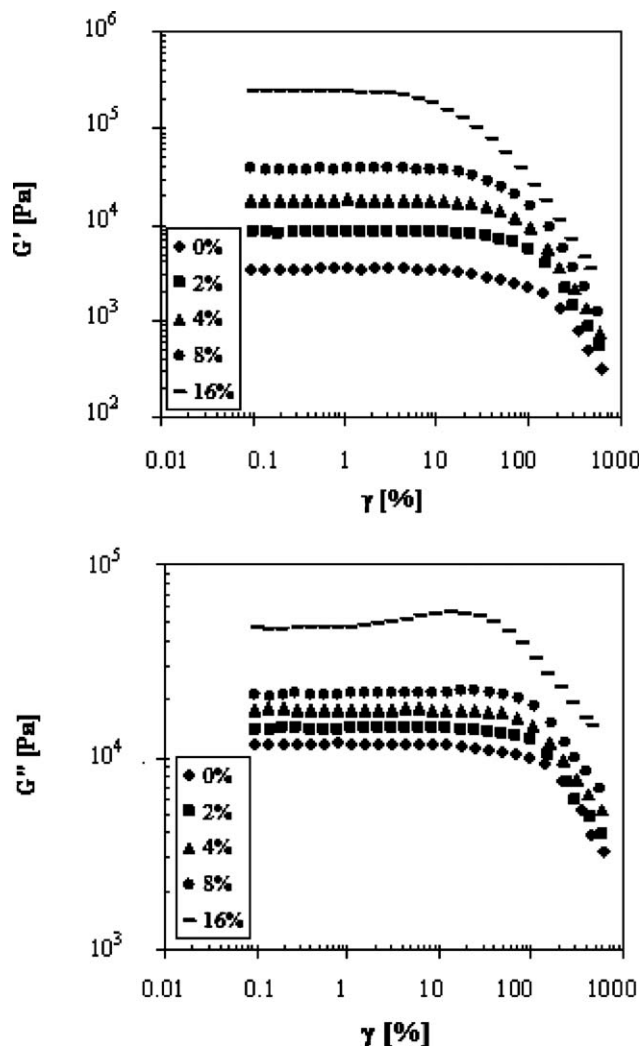


Figure 3. Storage and loss moduli of ABS/SiO₂ nanocomposites as a function of strain amplitude with different 20-nm particle loadings at 200°C ($\omega = 1$ rad/s).

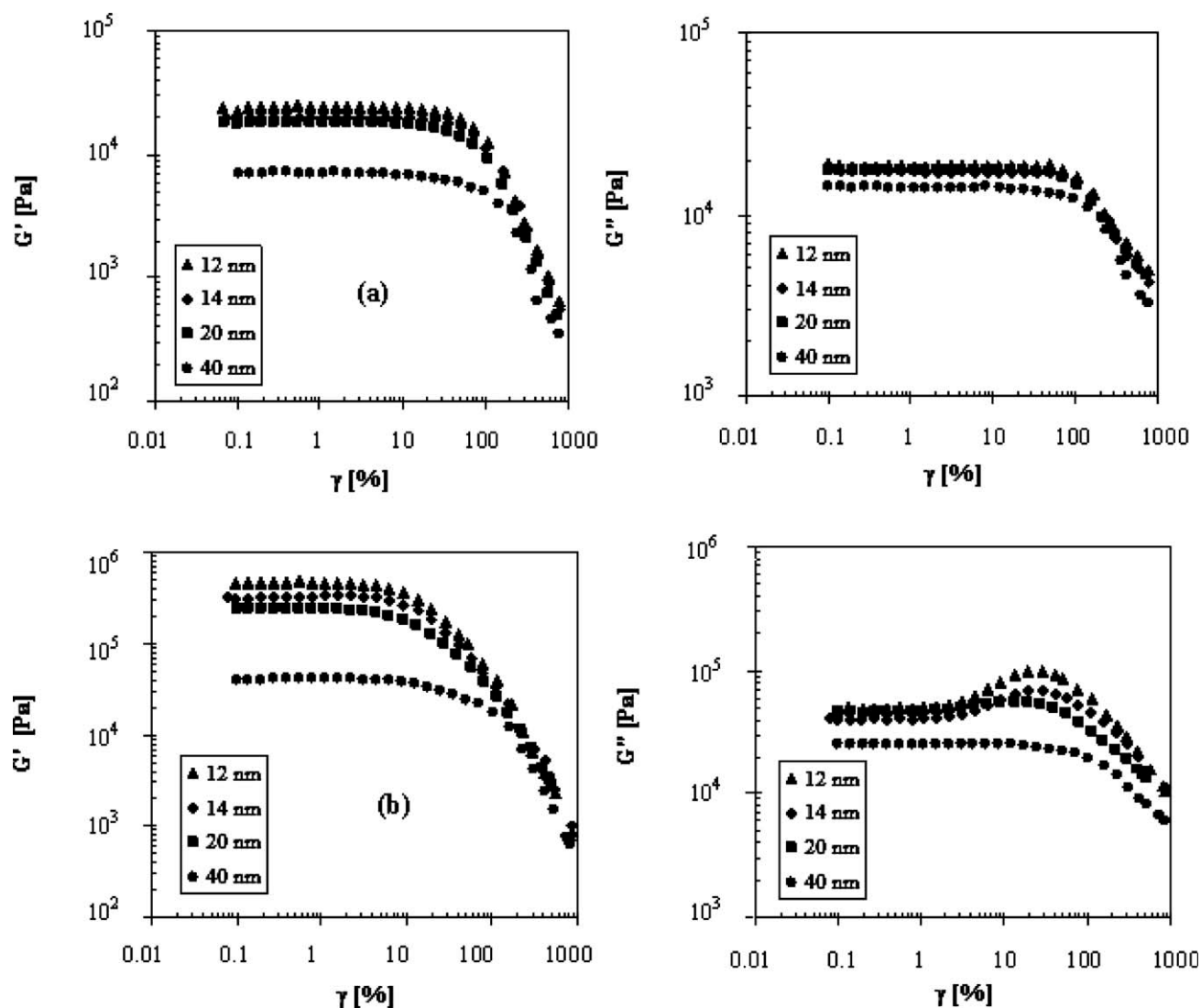


Figure 4. Storage and loss moduli of ABS/SiO₂ nanocomposites with different nanoparticle sizes, as a function of strain amplitude at 200°C ($\omega = 1$ rad/s): (a) 4 wt % and (b) 16 wt %.

nanocomposite. Furthermore, higher nanoparticle concentrations in the composite cause more polymer–particle interactions and increase adsorption of polymer chains on nanoparticles. Figure 3 shows the storage and loss moduli of nanocomposites as a function of strain. In all of the curves, both the linear and the nonlinear regions are seen. Increasing filler loading, the storage and loss moduli are enhanced, the slope of the nonlinear part increases, and the length of linear region decreases. Nonlinear viscoelastic behavior is intrinsic to the polymer matrix and is enhanced by the presence of the fillers,²⁰ owing to the changes of the polymer matrix structure by formation of nanoparticle agglomerations, adsorption of polymeric chains on nanoparticles, and increase of chain entanglements. In the low filler loading range, the storage and loss moduli are more influenced by polymer chain adsorption than filler network production. As filler concentration increases, more and stronger agglomerates are produced as a result of smaller interparticle

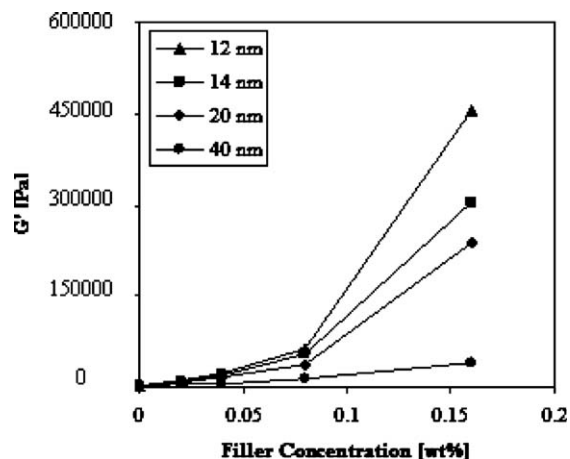


Figure 5. Storage modulus of ABS/SiO₂ nanocomposites with different nanoparticle sizes as a function of the filler concentration at 200°C ($\gamma = 1\%$, $\omega = 1$ rad/s).

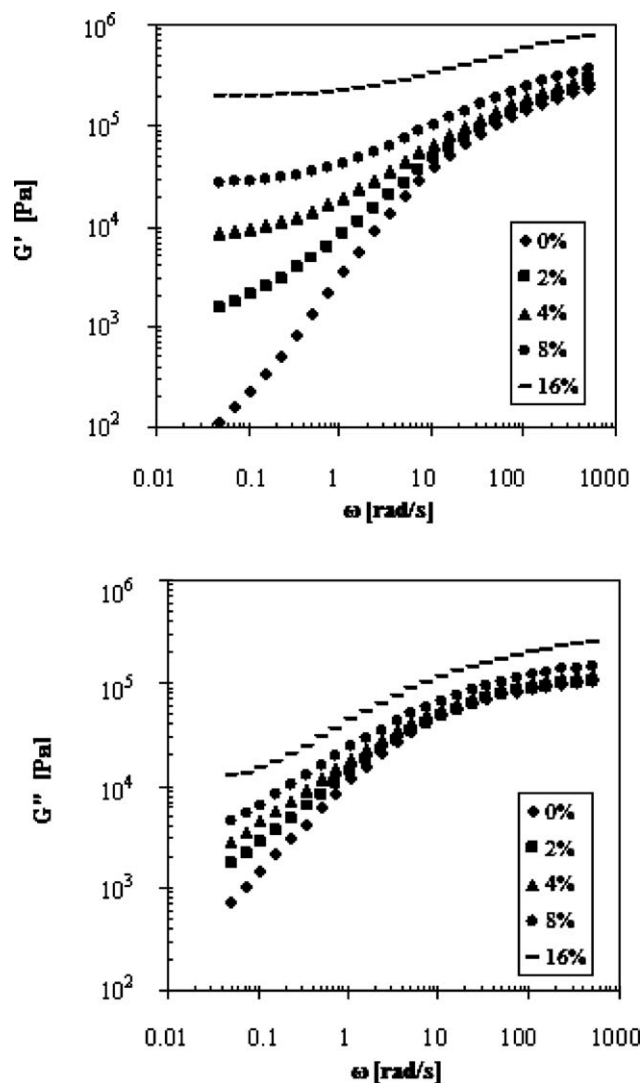


Figure 6. Storage and loss moduli of ABS/SiO₂ nanocomposites at different weight percents of 20-nm silica particles as a function of angular frequency at 200°C ($\gamma = 1\%$).

distances. Accordingly, the network structure becomes the most important mechanism controlling the rheological properties of composites with high nanoparticle concentration. As shown in Figure 3, the difference between the curves shows that the storage and loss moduli are less sensitive to filler concentration at high-strain than low-strain amplitudes. Therefore, both these moduli are reduced from a constant value to lower values by increasing deformation owing to the destruction of nanoparticle networks. Moreover, the difference between the curves is clearer in the low-strain region, where the filler network is less disrupted than at high strains.

As observed by other authors,^{9,10,14,21} the behavior of loss modulus is similar to that of storage modulus, but with a maximum near a critical strain in the G'' -curve. Aranguren et al.²¹ observed a maximum in loss modulus for nanocomposites of PDMS and untreated silica and they assumed this overshoot to

be related to energy dissipation produced by the breakdown of silica aggregates. In the present study, for nanocomposites with 20-nm silica, the maximum is seen only in the nanocomposite with 16 wt % silica, which contains a lot of filler agglomerates and aggregates.

Figure 4 shows the storage and loss moduli of the ABS/SiO₂ nanocomposites at 4 and 16 wt % loading of nanosilica with different sizes, as a function of strain amplitude. Reduction of particle size leads to the enhancement of surface area and surface energy so that the viscoelastic properties are intensified through creation of a network structure within the nanocomposites. The nanocomposites with smaller nanoparticles have higher storage and loss moduli, but the plateau region length is shorter for these nanocomposites. Reduction of moduli in the large strain region is more effective with decreasing nanoparticle

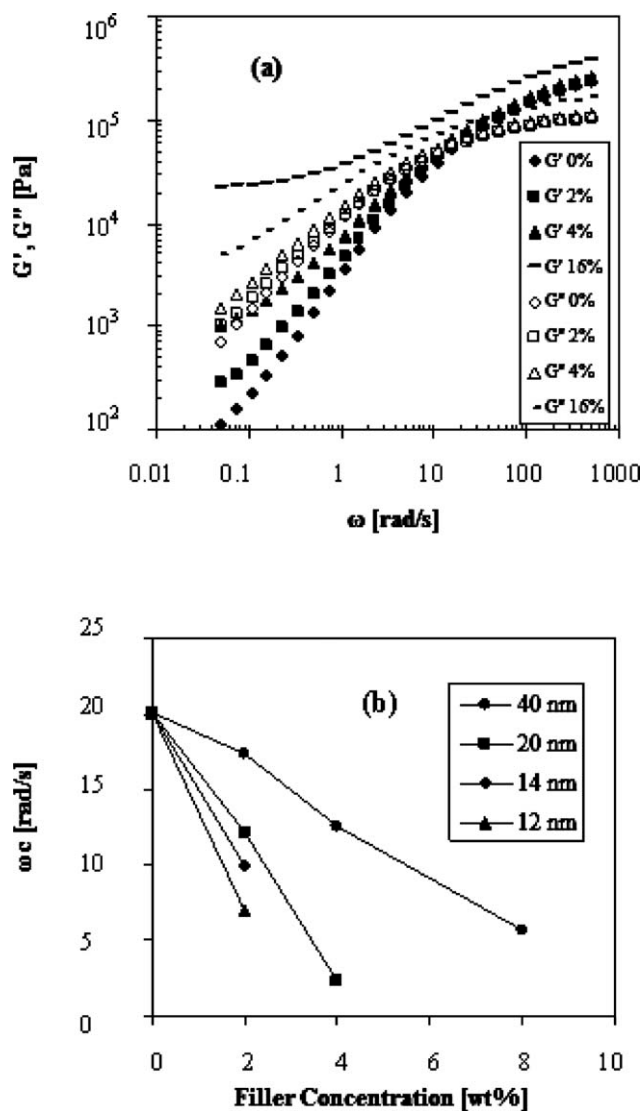


Figure 7. (a) Storage and loss moduli at different weight percent contents as a function of angular frequency and (b) Crossover frequency of G' and G'' as a function of filler concentration for ABS/SiO₂ nanocomposites with 40-nm silica particles at 200°C ($\gamma = 1\%$).

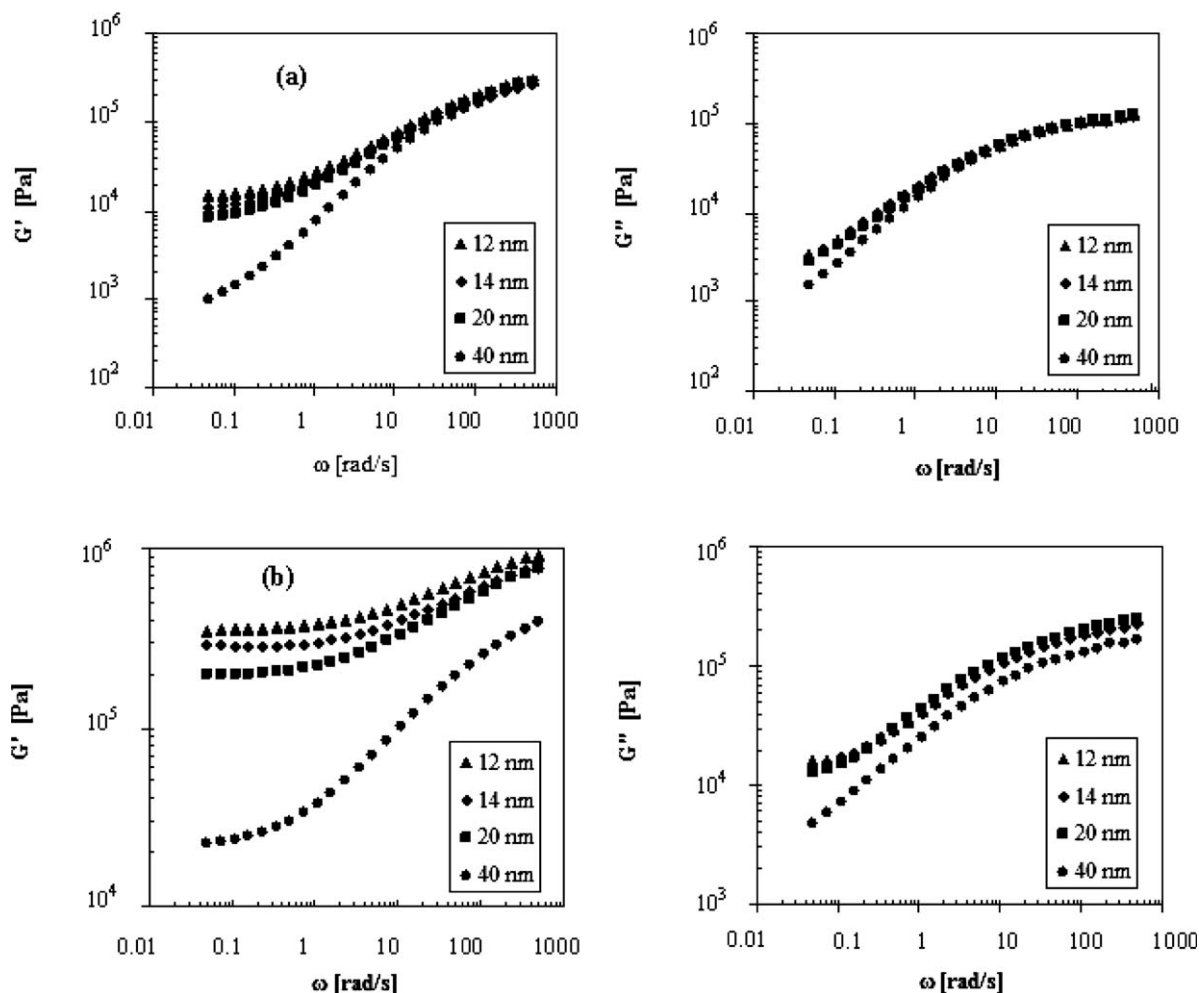


Figure 8. Storage and loss moduli of ABS/SiO₂ nanocomposites with different nanoparticle sizes, as a function of angular frequency at 200°C ($\gamma = 1\%$): (a) 4 wt % and (b) 16 wt %.

size, owing to the destruction of the large number of agglomerates. As shown in Figure 4, the moduli increase with reduction of nanoparticle size from 40 to 20 nm is greater than with size reduction from 20 to 12 nm. A decrease in nanoparticle size from 40 to 20 nm results in moduli increase because more polymer chains are adsorbed at nanoparticles and the strength of nanoparticle agglomerates increases as a result of a greater number of nanoparticles. By reduction of nanoparticle size from 20 to 12 nm, the nanoparticle number density increases greatly and the interactions between particles intensify resulting in stronger agglomerates that cause enhancement of moduli and prevent polymer chain adsorption by nanoparticles. As shown in Figure 4, there is not any maximum in G'' for nanocomposites with 4 wt % of any particle size studied. However, a maximum appears in nanocomposites with 16 wt % of particles and it intensifies with nanoparticle size reduction through dissipation of increasing energy.

Figure 5 shows that the rate of increase of the storage modulus with filler concentration at low strains is nearly independent of the filler size for low concentrations. This independency is more evident for nanocomposites with larger size particles, because

the internal structure of nanocomposites is more affected by smaller particles. One should also note that a stronger dependency on filler size exists at high nanoparticle concentrations.

The storage and loss moduli represented against frequency, for nanocomposites with different filler loadings of silica, are shown in Figure 6. For low filler concentrations, both G' and G'' grow with increasing frequency. In the low-frequency region, the storage modulus decreases monotonically with frequency from $\omega^{1.128}$ for neat ABS to $\omega^{0.036}$ for the nanocomposite with 16 wt % of 20-nm silica. The formation of a network structure in the composites at higher filler concentrations induces solid-like rheological behavior. Frequency-independent moduli are characteristic of solid-like behavior and indicate that the polymer chain reptation is slow owing to topological restraints owing to the inclusion of nanoparticles, and the clusters also present larger obstacles than the primary particles, and an increase in relaxation time results.²² As shown in Figure 6, the terminal plateau is clearly observed in nanocomposites with 16 wt % of silica.

A crossover frequency, ω_c , for G' and G'' is shown in Figure 7 for the neat ABS; however, the shift in crossover frequency

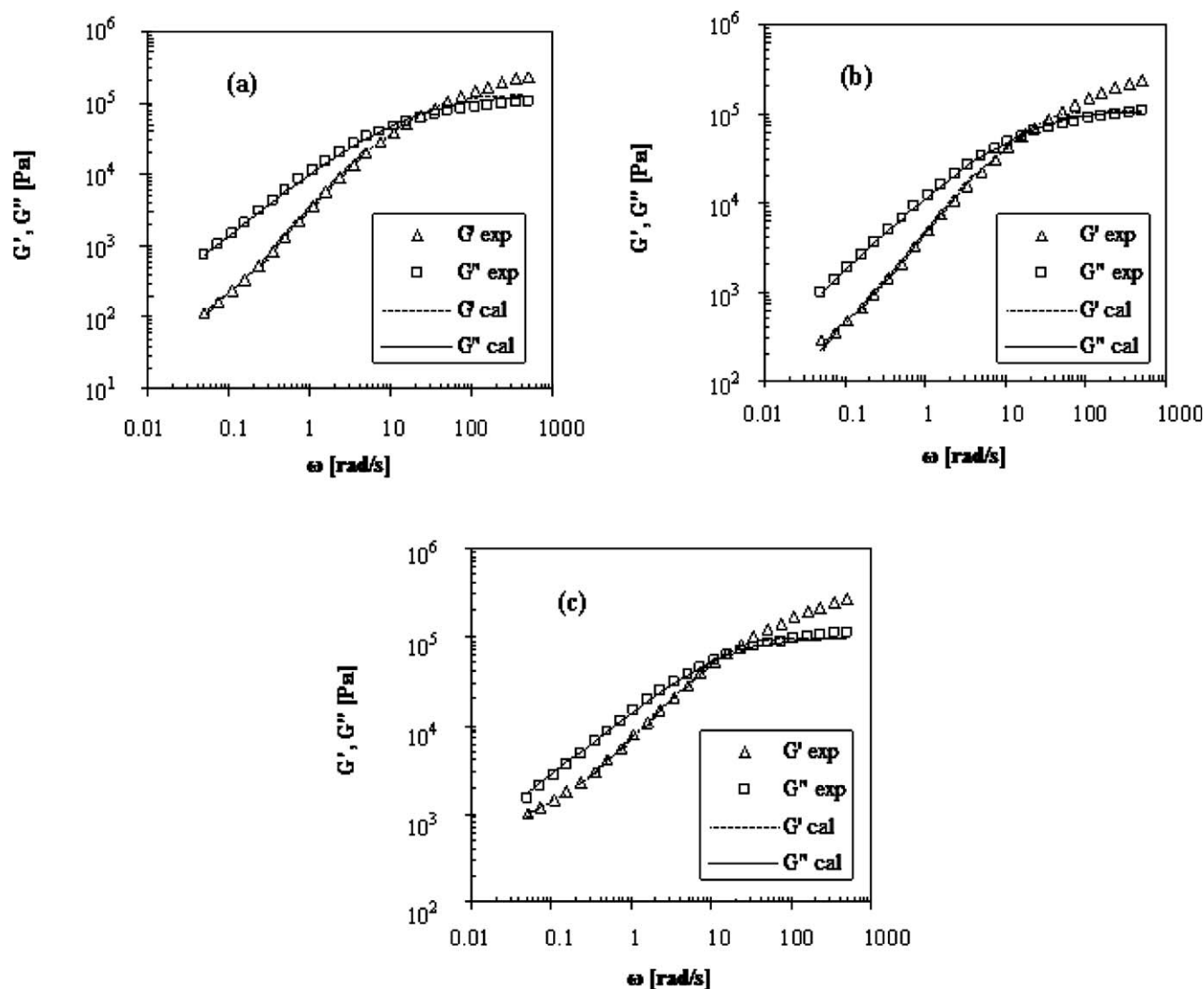


Figure 9. Comparison between experimental and simulated frequency dependencies of storage and loss moduli for ABS composite with (a) 0, (b) 2, and (c) 4 wt % of 40-nm silica particles.

toward lower values is presented as the loading of nanoparticles 40 nm increases. G' and G'' do not cross each other as the loading of nanoparticles increases more than 8 wt %. The ω_c is proportional to the inverse of the fluid's characteristic relaxation time λ_c , roughly the longest relaxation time.⁸ At higher loading, a decrease of ω_c leads to less flexibility of polymer chain so that it leads to the enhancement of λ_c by increasing nanoparticle loading.

Figure 8 shows the storage and loss moduli of the nanocomposites of ABS with 4 and 16 wt % of SiO₂ with different average diameters. As one can see with decreasing nanoparticle size, the storage modulus increases in the low-frequency region; however, at high frequencies, the changes become weak. The reduction of average particle size has the same effect as increasing filler loading. As a result, a solid-like behavior is observed for all nanocomposites with 16 wt % of every studied size of nanosilica, but for samples with 4 wt % of nanosilica, the solid-like behavior is just barely seen for 12-nm nanoparticles.

Sodeifian and Haghtalab²³ applied a Generalized Maxwell model for the correlation of the storage and loss moduli of PVC/NBR blends; in this study, we follow the same procedure to obtain a relaxation spectrum for ABS/SiO₂ nanocomposites. Thus, using a nonlinear regression method, the parameters of the relaxation spectrum are calculated through the generalized Maxwell model as

$$G'(\omega) = \sum_{i=1}^N \frac{G_i(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2} \quad \text{and} \quad G''(\omega) = \sum_{i=1}^N \frac{G_i(\omega\lambda_i)}{1 + (\omega\lambda_i)^2} \quad (1)$$

$$\sigma = \sum_{j=1}^M \left(\frac{G_j^{(\text{Exp})} - G_j^{(\text{Cal})}}{G_j^{(\text{Exp})}} \right)^2 + \left(\frac{G_j^{(\text{Exp})} - G_j^{(\text{Cal})}}{G_j^{(\text{Exp})}} \right)^2 \quad (2)$$

where G_i and λ_i are the parameters of the discrete relaxation spectrum, M is the number of experimental data values, and N is the number of Maxwell elements. Nanocomposites of ABS/

Table I. Relaxation Times and Modulus Found from G' and G'' Data Obtained for 40-nm ABS/SiO₂ Nanocomposites with 40-nm Particles by Generalized Maxwell Model

ABS		ABS/SiO ₂ 2%		ABS/SiO ₂ 4%	
λ_i (s)	G_i (Pa)	λ_i (s)	G_i (Pa)	λ_i (s)	G_i (Pa)
15.0427	240	17.6432	451	26.4573	1374
1.2169	2949	1.8005	2659	2.1446	3401
0.2150	27091	0.2853	22651	0.3861	17870
0.0366	94096	0.0485	81738	0.0717	76044

SiO₂ at low nanoparticle loadings do not show solid-like behavior in the low-frequency region and hence the Generalized Maxwell model can be used to describe their behavior. As Figure 9 shows, the experimental results are fitted with the model for the neat polymer and nanocomposites with 2 and 4 wt % of 40-nm

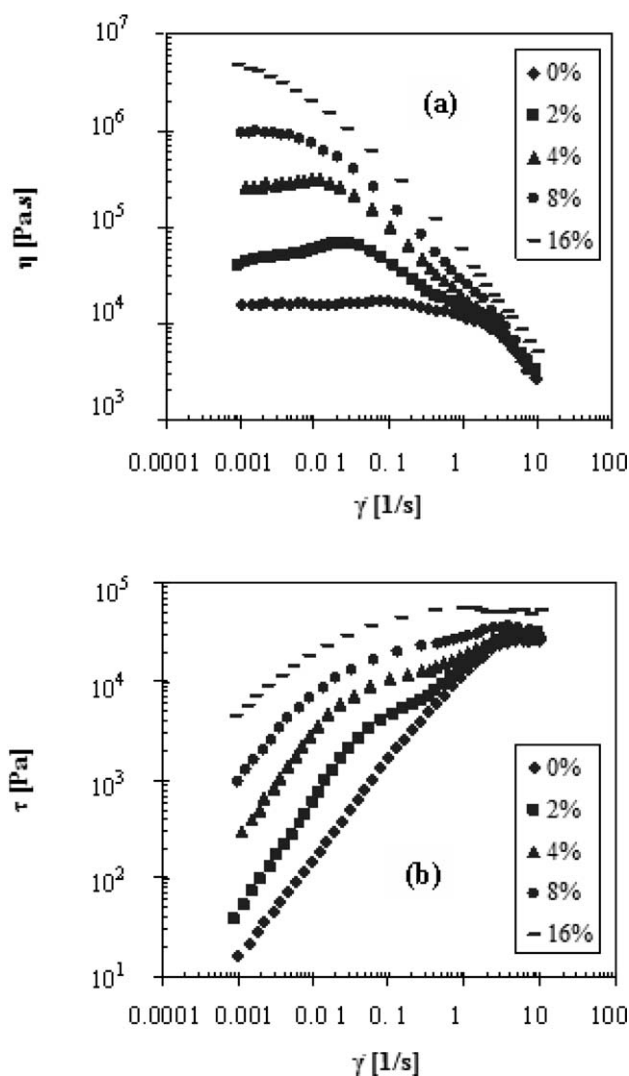


Figure 10. Viscosity and shear stress as a function of shear rate for ABS/SiO₂ nanocomposites with different 20-nm particle loadings at 200°C.

silica. The parameters of the discrete relaxation spectrum are listed in Table I. As would be expected, the results show that adding nanoparticles to the neat polymer leads to increasing relaxation time parameter values.

The adsorption of polymeric chains on nanoparticles and increasing occurrence of chain entanglements reduces polymer chain flexibility, leading to higher relaxation times. It should be noted that the maximum number of the Maxwell elements for G' and G'' of ABS/SiO₂ nanocomposites with more than 4 wt % silica may not increase beyond four, otherwise negative or zero spectrum parameter values result, because these samples behave closely to a viscoelastic solid, whose behavior, the Maxwell model, cannot adequately describe.

Figure 10 shows the viscosity and shear stress as a function of shear rate for the ABS/SiO₂ nanocomposites with different filler loadings. Neat ABS shows a wide Newtonian region;

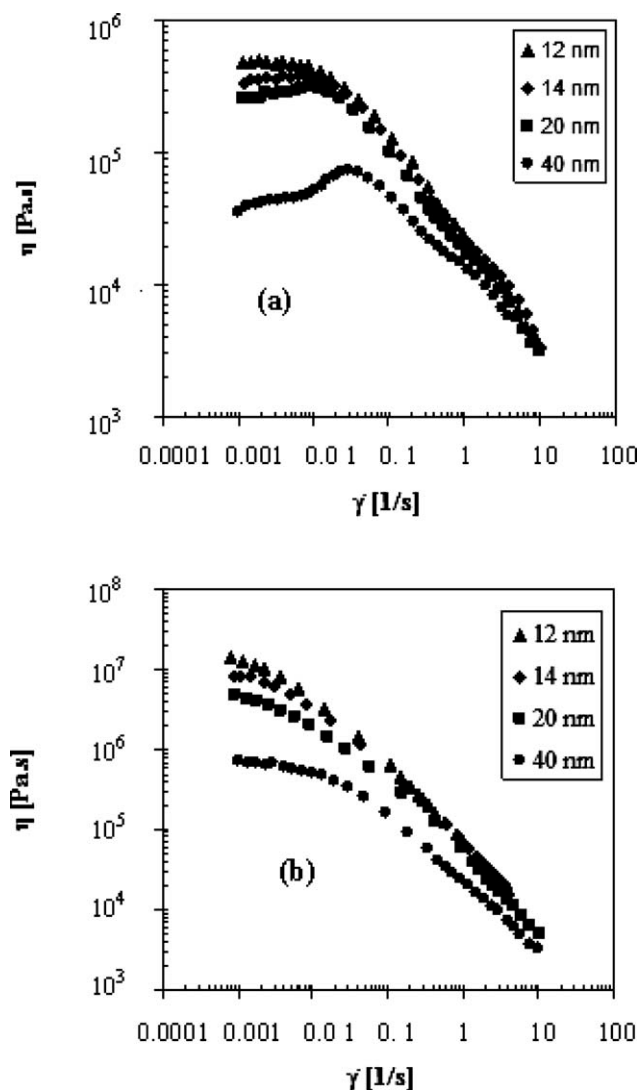


Figure 11. Viscosity of ABS/SiO₂ nanocomposites at (a) 4 and (b) 16 wt % of nanosilica with different sizes, as a function of the angular frequency at 200°C.

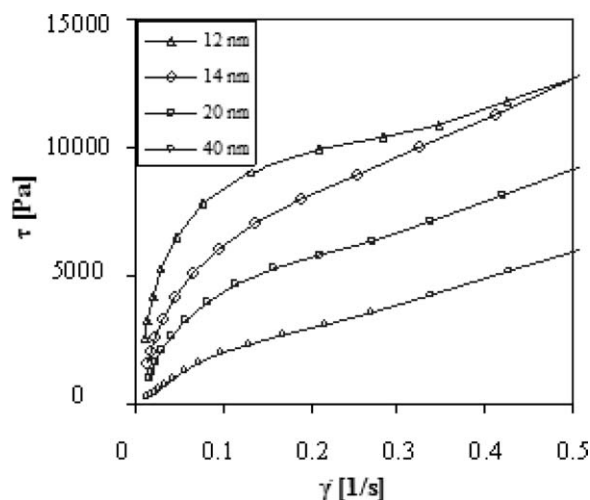


Figure 12. Shear stress as a function of shear rate for nanocomposites of ABS/SiO₂ with 2 wt % of different size nanoparticles at 200°C.

however, the length of this region decreases with increasing nanoparticle content, and eventually disappears for the highest filler concentration. Increasing filler content leads to shear thinning behavior at lower shear rates. The shear thinning behavior in the neat ABS is owing to the molecular orientation of the ABS matrix, whereas this behavior appears in nanocomposites as a result of both of the polymer chain orientation and disruption of filler networks in the sample. It is evident that for nanocomposites with 2 and 4 wt % of 20-nm silica, at the yield point the viscosity increases and then decreases before appearance of shear thinning behavior. Jianga et al.⁷ observed this behavior for ABS/CaCO₃ nanocomposites and concluded that the increase of viscosity indicated yield behavior of the filler network structure. They also noted that on the shear stress–shear rate curve, the slopes before and after the yield point originated from different rheological nature. Before the point, the slope was attributed to the combined effect of the elastic modulus of the sample and the property (spring factor) of the torque measuring spring of the rheometer. According to them, after the yield point the sample starts flowing and the curve gives the true rheological property of the sample. We believe that this interpretation is also valid for ABS/SiO₂ nanocomposites.

As mentioned before, smaller nanoparticles cause larger increases on the viscoelastic properties of nanocomposites. Figure 11(a) shows the viscosity of 4 and 16 wt % nanocomposites of ABS/SiO₂ with different nanoparticle sizes, as a function of shear rate. The nanoparticles of silica with 12 nm average size have 200 m²/g surface area and a high particle number density so that the reduction of the Newtonian region is intense, and completely disappears in the case of 16 wt % nanocomposites. However, the nanosilica with 40 nm average particle size and 50 m²/g surface area do not have such an intense effect on the polymer matrix for the same loading. Moreover, the slope in the shear thinning region increases as a result of nanoparticle size reduction. As can be seen, the Newtonian region is com-

pletely absent in Figure 11(b) for highly loaded nanocomposites.

Figure 12 shows the change of shear stress versus shear rate for 2 wt % nanocomposites with the different nanoparticle sizes. The shear stress increases with the reduction of particle size. One can also observe a change in the slope of the curves which corresponds to an overshoot in viscosity as shown in Figure 11. This behavior is more pronounced for nanocomposites with smaller nanoparticle size and shows that the yield behavior of nanoparticle networks is different in nanocomposites with fillers of different particle sizes.

CONCLUSIONS

The viscoelastic properties of ABS/SiO₂ nanocomposites with both different nanoparticle sizes and contents were obtained from the rheological measurements using parallel plate rheometry. Their properties were strongly dependent on nanofiller loading and nanoparticle size. For low filler loading, the mechanism of polymer chain adsorption on nanoparticles was dominant in enhancing the viscoelastic properties. However, at high filler loadings the viscoelastic properties were mostly controlled by a filler network formation rather than by the adsorption of polymer chains on the surface of nanoparticles. The buildup of filler networks intensified both the storage and the loss moduli and induced a solid-like behavior in nanocomposites at the low-frequency region. Furthermore, the disruption of networks with increasing shear rate leads to earlier and more effective shear thinning behavior in nanocomposites with higher filler loading and smaller particle size. The obtained parameters of a multimode Maxwell model for nanocomposites with nanofiller content up to 4 wt % showed that the relaxation times of polymer chains increase with nanoparticle content.

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