

Plasticization of Nano-CaCO₃ in Polystyrene/Nano-CaCO₃ Composites

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Received 29 December 2004; accepted 15 March 2005

DOI 10.1002/app.22752

Published online 6 December 2005 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The shear rheological properties of polystyrene (PS)/nano-CaCO₃ composites were studied to determine the plasticization of nano-CaCO₃ to PS. The composites were prepared by melt extrusion. A poly(styrene-butadiene-styrene) triblock copolymer (SBS), a poly(styrene-isoprene-styrene) triblock copolymer (SIS), SBS-grafted maleic anhydride (SBS-MAH), and SIS-grafted maleic anhydride were used as modifiers or compatibilizers. Because of the weak interaction between CaCO₃ and the PS matrix, the composites with 1 and 3 phr CaCO₃ loadings exhibited apparently higher melt shear rates under the same shear stress with respect to the matrix polymer. The storage moduli for the composites increased with low CaCO₃ concentrations. The results showed that CaCO₃ had some effects on

the compatibility of PS/SBS (or SBS-MAH)/CaCO₃ composites, in which SBS could effectively retard the movement of PS chain segments. The improvement of compatibility, due to the chemical interaction between CaCO₃ and the grafted maleic anhydride, had obvious effects on the rheological behavior of the composites, the melt shear rate of the composites decreased greatly, and the results showed that nano-CaCO₃ could plasticize the PS matrix to some extent. Rheological methods provided an indirect but useful characterization of the composite structure. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2138–2143, 2006

Key words: composites; nanoparticles; polystyrene; rheology

INTRODUCTION

The mixing of polymers with nanoscale inorganic particles has been recognized as a potential and economical method of producing new materials not only with enhanced mechanical properties, dimensional stability, and flame-retardant properties but also with various new functions. Polystyrene (PS) is a common resin used extensively in the plastic industry because of its excellent transparency and processing properties, but its brittleness restricts its application, especially the blending of PS with inorganic particles. The development of the production of inorganic nanoparticles such as nano-CaCO₃, nano-SiO₂, and nano-TiO₂ offers an opportunity to prepare PS nanocomposites without weakening the toughness. In the past decade, the preparation and properties of PS/clay nanocomposites and its blends have been intensively studied.^{1–7} Most of the studies have focused on high-impact polystyrene (HIPS)/nano-TiO₂,⁸ PS/CaCO₃,^{9–12}

PS/SiO₂,¹³ PS/graphite,^{14,15} and PS/carbon-nanotube composites.¹⁶ The mechanical properties of filled PS composites depend, to a great extent, on the filler size, shape, surface modification, and distribution in PS, the interfacial interaction and morphology, and so forth.

The rheological properties of polymer/inorganic nanoparticles are important for the fabrication of polymer nanocomposites and the application of melt-processing techniques. Because a lot of factors, such as the particle size, shape, structure, amount, and dispersion in the matrix, will affect the rheological properties of filled polymer nanocomposites, the study of rheology can offer us some indirect information on the nanocomposite structure and interaction between the nanoparticles and polymer matrix. Previous rheological studies of nanocomposites have involved some polymer/clay nanocomposites.^{17–20} Generally, the steady shear viscosity of both intercalated and exfoliated nanocomposites increases with the silicate loading, as shown by Krishnamoorti and coworkers^{21–23} for poly-(dimethylsiloxane-co-diphenylsiloxane), polystyrene-polyisoprene diblock copolymer, and end-tethered polymer layered silicate nanocomposites. Kim and White²⁴ investigated the rheological properties of suspensions of talc and calcium carbonate and their mixtures in a PS melt. The results showed that the shear viscosity decreased with increasing shear rate but increased with increasing particle loading. Galgali et

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Contract grant sponsor: Science and Technology Program of Guangzhou; contract grant number: 2002Z3-D2011.

Contract grant sponsor: Natural Science Important Program of Guangdong Province; contract grant number: 021731.

al.²⁵ reported that the solid-like rheological response in polypropylene/clay nanocomposites was independent of the finer structure of the nanocomposites but dependent on the frictional interactions between the silicate layers. The exfoliated layers could bridge different silicate crystallites to form a percolating network that strongly resisted deformation.

Some research is not very consistent with previous findings with conventionally filled polymer systems in which the additions of inorganic particles caused significant increases in the viscosity of the polymers. Solomon et al.²⁶ indicated in their studies on the rheology of polypropylene/clay hybrid materials modified by maleic anhydride (MAH) functionalized polypropylene that the storage modulus exhibited a complex dependence on the concentration of the clay. The data of the storage modulus for the highest frequencies monotonically increased with the particle loading; however, low-frequency data for the intermediate concentration from 2.03 to 4.10 wt % showed an inverse dependence on the particle loading. The authors thought that the lower molecular weight compatibilizer of the MAH-functionalized polypropylene could plasticize the polypropylene matrix, and MAH might promote chain scission of the neat polypropylene. Real differences in the clay structure and an effect of the particle loading on the phase behavior of the hybrids or the efficacy of the melt mixing could also be the reasons. A model of hairy platelets was proposed by Meincke et al.,¹⁸ who fully described the thinning effect of rheological behavior in the plateau region of exfoliated PS/layered silicates nanocomposites.

Chen et al.²⁷ in their studies of poly(*n*-butyl methacrylate) (PBMA)/calcium carbonate composites, reported that the modulus of a composite with 10% CaCO₃ was less than that of PBMA, as observed from the melting viscosity, as a result of the lack of adhesion and probable voiding at the interface between CaCO₃ and the matrix. Liang and a coworker^{28,29} revealed that acrylonitrile-butadiene-styrene (ABS) with 10% nano-CaCO₃ exhibited a lower viscosity and a higher melt flow rate (MFR) than pure ABS with increasing wall shear stress.

In this article, to investigate the plasticization of nano-CaCO₃ to a PS matrix, we focus on the rheological behavior of PS/nano-CaCO₃ composites and composites modified by poly(styrene-butadiene-styrene) triblock copolymer (SBS), poly(styrene-isoprene-styrene) triblock copolymer (SIS), SBS-grafted maleic anhydride (SBS-MAH), and SIS-grafted maleic anhydride (SIS-MAH) with nano-CaCO₃ concentrations less than 10 phr to investigate the effects of nanometer inorganic fillers, modifiers, and interactions between the particles and matrix on the rheological properties of nanoparticle-filled polymers.

EXPERIMENTAL

Materials and preparation

Polymer/nano-CaCO₃ composites were prepared with an SJ-30 single-screw extruder (Nanjing, China) with CaCO₃ concentrations of 0, 1, 3, 5, and 7 phr. The temperatures in the five zones of the extruder (from the hopper to the die) were 175, 195, 210, 210, and 200°C, respectively. The screw speed was 60 rpm, and the screw length/diameter ratio of the extruder was 30. The polymer used as the matrix in this study was PS (Polytac PG-33, a general grade resin supplied by Chi Mei Corp.). MFR of PS (PG-33) was 7.8 g/10 min (ASTM D 1238, 200°C, 6.89×10^5 Pa). A nanoscale calcium carbonate with a diameter of 50–60 nm (CC-R, Shiraishi Kogyo Kaisha, Ltd.) was used as the filler. A polystyrene-butadiene-polystyrene triblock copolymer (SBS-788; styrene-to-butadiene weight ratio = 30/70, MFR = 5.07 g/10 min) and a polystyrene-isoprene-polystyrene triblock copolymer (SIS-1209; styrene-to-isoprene weight ratio = 30/70, MFR = 6.25 g/10 min) were supplied by Baling Petroleum, Ltd., of Sinopec Corp. The compatibilizer SBS-MAH was prepared by a chemical reaction in toluene initiated by benzoyl peroxide; the molar ratio of grafted MAH to the butadiene unit was 2.22 mol %, and it was abbreviated to SBS-2.22MAH. SIS-MAH with 2.11 mol % grafted MAH was produced by melt extrusion with dicumyl peroxide serving as an initiator, and it was abbreviated to SIS-2.11MAH. The composite components are expressed as weight ratios in this article.

Rheology measurements

Rheology measurements of the shear flow at high shear rates were performed on an XYL-II (Jilin University, Jilin, China), a simple piston-type capillary rheometer including two dies with capillary diameters of 1.0 and 0.5 mm and length/diameter ratios of 40 and 72, respectively. The wall shear rate ($\dot{\gamma}_w$), varying from 10 to 10² s⁻¹, and shear flow were measured at 190 and 230°C. $\dot{\gamma}_w$ is defined as $\dot{\gamma}_w = 4Q/(\pi R^3)$, where Q is the total volume flow rate and R is the capillary radius.

The shear stress at the capillary wall is $\tau_w = \Delta P R / 2L$, where ΔP is the total pressure on the melt polymer in the capillary and the capillary length is L . The L/R ratio is large enough to neglect the entrance correction of the pressure drop.

Dynamic mechanical analysis

Dynamic mechanical analysis was performed in the single-cantilever mode between -110 and 130°C at frequencies of 1, 10, and 100 Hz with a 10- μ m amplitude (DMA2980 dynamic mechanical analyzer, TA In-

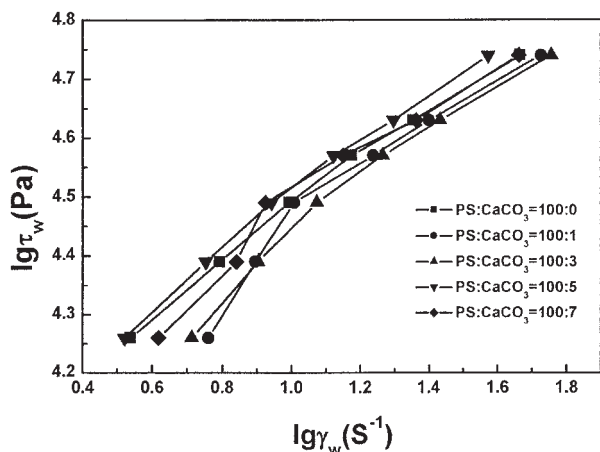


Figure 1 Shear-rate dependence of the shear stress for PS (PG-33) and its calcium carbonate composites at 190°C.

struments). Test samples were prepared by injection molding.

Vicat soft temperature

The Vicat soft temperature was measured on a ZWK-6 testing machine (Shenzhen SANS Testing Machine Co., Ltd.) at a heating rate of 50°C/h; the pressure was 50 N. Test samples were prepared by injection molding.

RESULTS AND DISCUSSION

Rheological properties of the PS composites

Polymers are viscoelastic materials; above the melting range, they also exhibit evidence of elasticity. PS is known as a pseudoplastic resin, and the presence of nanometer inorganic particles may have some effects on its flow behavior. Figures 1 and 2 plot the shear-rate dependence of τ_w for pure PS and its calcium carbonate composites at 190 and 230°C, respectively, the CaCO_3 concentrations varying from 1 to 7 phr. The composites with CaCO_3 concentrations lower than 5 phr showed a higher flow rate than PS under the same shear stress; thinning effect for the 3 phr CaCO_3 composite was more obvious. The flow curve indicated that the nano- CaCO_3 with less than 3 phr had some effects on plasticizing the PS matrix.

The rheological properties of PS composites with CaCO_3 loadings less than 3 phr are not agreement with the normal viewpoint that the addition of inorganic particle fillers causes significant increases in the viscosity of a polymer, except for composites in which the CaCO_3 concentration was greater than 5 phr in this study. A possible explanation may be as follows. First, nano- CaCO_3 is hydrophobic and can disperse very well in the PS matrix, so the particle concentration is

low enough to reduce the interaction between CaCO_3 particles. Nano- CaCO_3 may also promote chain scission of neat PS. Second, because of a lack of efficient interactions between CaCO_3 particles and PS, the interfacial strength of the composites is also weak. Because each contributed to the reduction in the viscosity of the matrix in which the nanometer particles were dispersed, the composites with certain contents of CaCO_3 exhibited better flowability than pure PS in this study. Nano- CaCO_3 can plasticize the PS matrix to some extent. Liang and a coworker^{28,29} in their studies on the MFR of ABS/ CaCO_3 showed that ABS with 10% nano- CaCO_3 exhibited lower viscosity and a higher MFR than pure ABS with increasing wall shear stress. Chen et al.²⁷ explained in research of PBMA/ CaCO_3 composites that the melting viscosity with 10% CaCO_3 was less than that of PBMA because of the lack of adhesion and probable voiding at the interface between CaCO_3 and the matrix.

PS/SIS blends with 2 phr SIS to modify the brittleness of PS exhibited a thinning effect with increasing shear stress, as shown in Figure 3. Because of the entanglement between PS chains and polybutadiene units, PS/SIS displayed a lower flow rate when the shear stress was low, but it was more sensitive to the shear stress than pure PS because of the flexibility of SIS. An additional improvement in the flowability was found when a small amount of nano- CaCO_3 was mixed with the PS/SIS blends, especially in the PS/SIS composites with a 1 phr CaCO_3 loading. The plasticization effect of nano- CaCO_3 in the PS/SIS blends was more obvious than that of pure PS, perhaps because of the dispersion of CaCO_3 whether in the SIS domain or in the PS domain and the compatibility between PS and SIS. Dynamic mechanical analysis will offer some further illustration.

The rheological behaviors of the PS/SBS blends are also exhibited in Figure 4. The results differ from SIS-toughened PS and its composites; the plasticizing

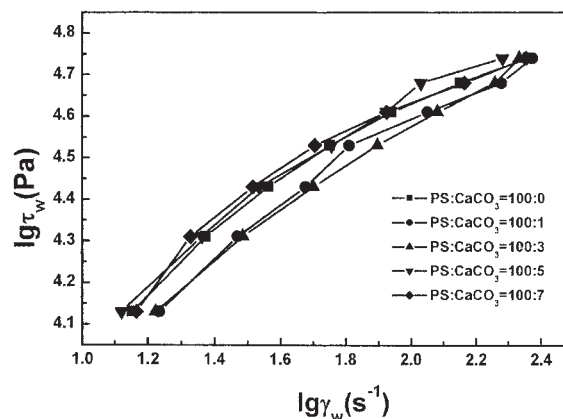


Figure 2 Shear-rate dependence of the shear stress for PS (PG-33) and its calcium carbonate composites at 230°C.

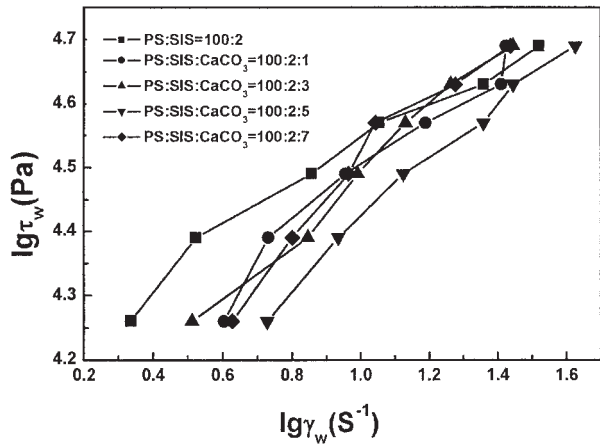


Figure 3 Shear-rate dependence of the shear stress for PS/SIS blends and their calcium carbonate composites at 190°C.

effect of nano-CaCO₃ on PS was not found in these composites. To explain this phenomenon, additional experiments are required to determine the different effects of the particle loading on the structure of the polymer matrix and its blends.

Effects of the chemical interaction on the rheology

It is reasonable to hypothesize that the surface interactions between CaCO₃ and the polymer matrix would affect the rheological properties of the composites. The possible effects of the chemical bond interactions on the rheology were investigated by the preparation of SIS-MAH and SBS-MAH, which could be used as compatibilizers. The change in the shear rate of the composites with different MAH concentrations is reported in Figure 5. Grafted MAH in SIS or SBS chains led to a large decrease in the shear rate of the PS/SIS-MAH/CaCO₃ and PS/SBS-MAH/CaCO₃ composites with respect to the composites not contain-

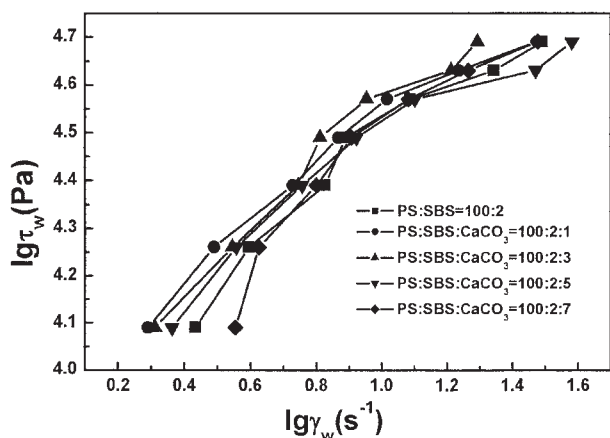


Figure 4 Shear-rate dependence of the shear stress for PS/SBS for PS/SBS/CaCO₃ composites at 190°C.

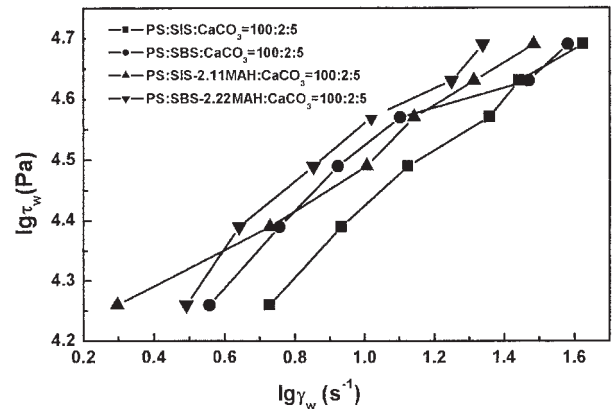


Figure 5 Effects of grafted MAH on the flow properties of PS composites at 190°C.

ing MAH. Because of the stronger chemical interaction between MAH and polar groups such as —OH existing on CaCO₃ surfaces and the coordination of Ca²⁺ ions to MAH, the compatibility of SIS, SBS, and CaCO₃ increased. The rheology measurements revealed the extreme sensitivity of the flow response to the interaction or the compatibility between the inorganic particle filler and polymer matrix.

The temperature dependence of the storage and loss moduli of PS composites with 1 and 3 phr CaCO₃ loadings and pure PS are plotted in Figure 6. The increase in the storage and loss moduli due to the addition of CaCO₃ is obvious, especially for the com-

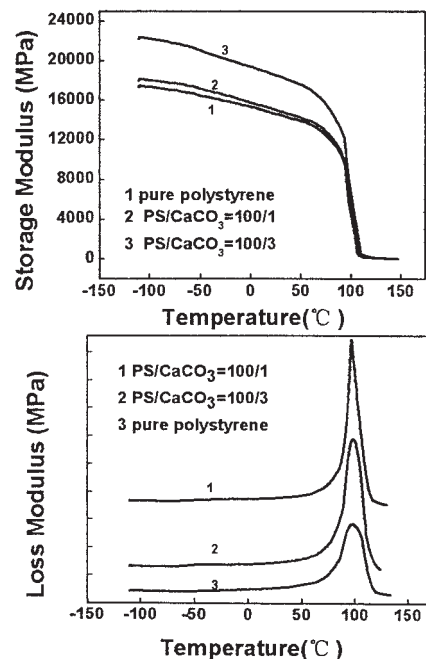


Figure 6 Temperature dependence of the storage and loss moduli of PS and its composites as determined by dynamic mechanical analysis at an oscillatory frequency of 10 Hz.

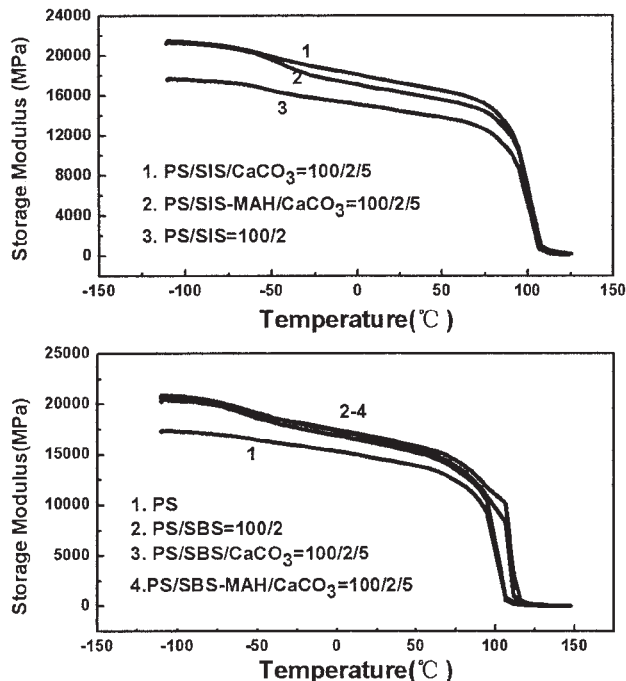


Figure 7 Temperature dependence of the storage modulus of PS/SIS, PS/SBS, and their composites as determined by dynamic mechanical analysis at an oscillatory frequency of 10 Hz.

posite with 3 phr CaCO_3 filler. The temperature at the peak value of the loss modulus corresponding to the cooperative motion of PS chain segments varied from 97.1 to 96.7°C for 1 phr CaCO_3 and to 98.1°C for 3 phr CaCO_3 /PS composites at an oscillatory frequency of 10 Hz. However, for 100 Hz, a reduction of the peak-value temperature from 109.8 to 102.0°C corresponding to pure PS and 3 phr CaCO_3 /PS composites was found. The results revealed the weak interaction between CaCO_3 and the matrix. The chain scission of pure PS by nano- CaCO_3 at a high oscillatory frequency would contribute to the reduction in the peak-value temperature of the loss modulus. The results can further explain the enhancement of the shear flow rate of PS/ CaCO_3 composites, as shown in Figure 2.

SIS and SBS have different effects on PS moduli: 2 phr SBS led to a larger enhancement of the storage modulus in comparison with SIS, and CaCO_3 caused another greater increment in the moduli of the PS/SIS and PS/SBS blends, as shown in Figure 7. As for the temperature at the peak value of the loss modulus of PS, 2 phr CaCO_3 showed no apparent influence on it for PS/SIS/ CaCO_3 and PS/SIS-MAH/ CaCO_3 composites, as shown in Figure 8. However, some obvious changes in the peak-value temperature of the loss modulus were observed for SBS- and SBS-MAH-modified PS and PS/ CaCO_3 composites, as plotted in Figure 9. SBS could effectively retard the movement of PS chain segments, and the peak-value temperature of

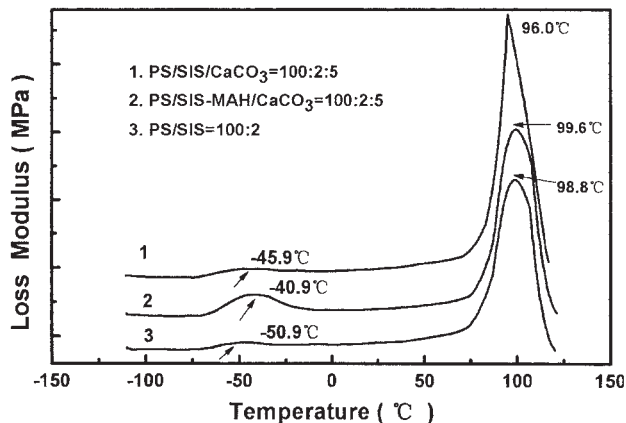


Figure 8 Temperature dependence of the loss modulus of PS/SIS blends and their composites as determined by dynamic mechanical analysis at an oscillatory frequency of 10 Hz.

the loss modulus increased from 97.1°C for pure PS to 101.7°C for the PS/SBS blends. These differences between SIS- and SBS-modified composites may be related to the CaCO_3 dispersion tendency; that is, in the PS/SIS/ CaCO_3 and PS/SIS-MAH/ CaCO_3 composites, CaCO_3 dispersed mainly in SIS or SIS-MAH domains or at the interface and led to an increase in the peak-value temperature of the loss modulus, which was related to the isoprene domain. However, in PS/SBS/ CaCO_3 and PS/SBS-MAH/ CaCO_3 composites, a close-up of the peak-value temperature of the loss modulus corresponding to the PS and SBS domains, respectively, implies that CaCO_3 maybe had some effect on the compatibility of the composites. The difference in the compatibility and how the CaCO_3 dis-

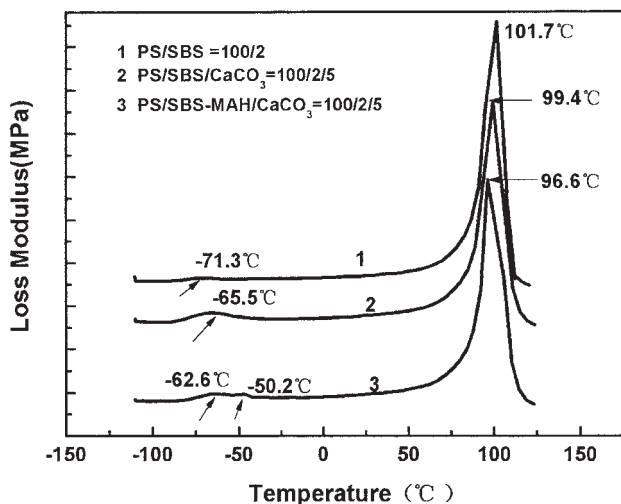


Figure 9 Temperature dependence of the loss modulus of PS/SBS blends and their composites as determined by dynamic mechanical analysis at an oscillatory frequency of 10 Hz.

TABLE I
Vicat Soft Temperature of PS and Its Composites

| | PS | PS/CaCO ₃ composites | | | |
|-----------------------------|------|---------------------------------|-------|-------|-------|
| Content ratio (w/w) | | 100:1 | 100:3 | 100:5 | 100:7 |
| Vicat soft temperature (°C) | 84.5 | 85.0 | 84.8 | 84.3 | 84.0 |

persed in the composites could affect the rheological properties of the composites, as shown in Figures 3–5.

Vicat soft temperature

Table I displays the Vicat soft temperature of pure PS and its CaCO₃ composites. A low concentration of nano-CaCO₃ did not improve the resistance to deformation of the composites; the weak interaction between CaCO₃ and the PS matrix may have contributed to the results.

CONCLUSIONS

The PS/nano-CaCO₃ composites with 1 and 3 phr CaCO₃ loadings exhibited apparently higher melt shear rates under the same shear stress with respect to the matrix polymer because of the plasticization of nano-CaCO₃ to the PS matrix. The composite storage modulus increased with low concentrations of CaCO₃. Nano-CaCO₃ had some effects on the compatibility of the PS/SBS (or SBS-MAH)/CaCO₃ composites, in which SBS could effectively retard the movement of PS chain segments. The improvement of the compatibility due to the chemical interaction between CaCO₃ and grafted MAH had obvious effects on the rheological behavior of the composites, and the melt shear rate of the composites decreased greatly. In conclusion, the rheological properties of PS composites filled with nano-CaCO₃ are sensitive to the inorganic particle dispersion, content, surface modification, interaction in the interface, and matrix features; rheological meth-

ods can provide an indirect but useful characterization of the composite structure.

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