Macromolecules
ARTICLE

Macromolecules **2011**, *44*, 1177–1181 **1177**
DOI: 10.1021/ma102631h

Further Consideration of Viscoelastic Two Glass Transition Behavior of Nanoparticle-Filled Polymers

Christopher G. Robertson* and Mindaugas Rackaitis

Bridgestone Americas, Center for Research and Technology 1200 Firestone Parkway, Akron, Ohio 44317-0001, United States

Received November 18, 2010; Revised Manuscript Received December 10, 2010

ABSTRACT: Tsagaropoulos and Eisenberg [*Macromolecules* **1995**, *28*, 396; *Macromolecules* **1995**, *28*, 6067] reported a second loss tangent (tan δ) peak in temperature-dependent viscoelastic data for various un-cross-linked polymers filled with nanometer-sized silica particles. This peak, occurring at temperatures as much as 100 °C above the primary tan δ peak (glass-to-rubber softening transition), was ascribed to the glass transition of immobilized chains near the particles. This research is often cited as support for the existence of severely retarded segmental motion of polymer near the surfaces of small particles (glassy polymer shell). We offer a different interpretation of the results from Tsagaropoulos and Eisenberg, reinforced by our recent measurements on particle-filled polybutadiene and consideration of other literature data. Particles restrict the flow of some polymer chains, thus resulting in incomplete terminal relaxation, and partial cross-linking of unfilled polymers produces the same higher temperature tan δ peak. Polymer chains which are adsorbed onto filler surfaces are immobilized from a flow relaxation (chain diffusion/reptation) standpoint, but segmental relaxation (glass transition) is not substantially altered by small particles as a general rule.

Introduction

The effects of nanoconfinement, free surfaces, and interaction with particles on the glass transition of polymers have been reviewed in recent years with no general consensus revealed.[1−3] Concerning particle-induced effects, there are observations that the segmental relaxation (α-relaxation) and glass transition temperature (T_g) are largely unaffected by the presence of filler, despite significant levels of “bound” polymer enacted by high filler surface area and chemically modified interfaces.[4−9] Kumar, Gidley, and co-workers[10] recently used differential scanning calorimetry (DSC) and dielectric relaxation spectroscopy to probe the influence of 15 nm diameter silica particles on the glass transition of poly(2-vinylpyridine). This system has strong attractive interactions between polymer and filler, but even at a very high filler volume fraction (ϕ) of 0.5 (62.5 wt % filler) they noted a T_g increase of only about 5 °C. While this T_g shift corresponds to roughly a 2 decade increase in average segmental relaxation time given the typical activation energy range of polymers in the T_g temperature region, there was no evidence for a separate glass transition for the polymer near the particles. There are reports which show that filler can have a very significant influence on the segmental dynamics and T_g.[11−17] In particular, the research of Tsagaropoulos and Eisenberg[11,12] is often cited to support the notion that the glass transition can be greatly impacted by the filler. They observed a second tan δ peak in viscoelastic data for various nanoparticle-filled un-cross-linked polymers which was 60−100 °C above the main viscoelastic glass transition of the polymer, and this was attributed to the T_g of the polymer layer surrounding the particles. Given these striking and influential results, we study the viscoelastic response of polymers containing small particles to further investigate this behavior by considering our new data for polybutadiene reinforced with carbon black and studying other existing literature results for nanoparticle-filled polymers.

Experimental Details

A polybutadiene (PB) was synthesized by batch anionic polymerization of 1,3-butadiene in hexane solution using *n*-butyllithium as the initiator. After polymerization, the living polybutadiene solution was terminated and coagulated using 2-propanol, stabilized with an antioxidant, and dried. The microstructure of the polybutadiene was analyzed using ^{1}H and ^{13}C NMR (Varian Mercury 300 NMR) with deuterated chloroform as solvent. The polymerization of the 1,3-butadiene resulted in a statistical mixture of 8 mol % 1,2-addition, 54 mol % trans-1, 4-addition, and 38 mol % cis-1,4-addition. Gel permeation chromatography (GPC) was performed in tetrahydrofuran solvent using a Waters model 150-C with a refractive index detector. GPC measurements were conducted relative to polystyrene standards, and the results were then converted to absolute molecular weight information by applying the universal calibration approach using known intrinsic viscosity versus molecular weight control data for polybutadiene having the above backbone microstructure. From this GPC evaluation, it was determined that $M_n = 110$ kg/mol and $M_w/M_n = 1.06$ for this polymer.

Filled polymer compounds with 37.5 wt % carbon black (ϕ = 0.23) were formed by mixing polybutadiene and carbon black in a Brabender Prep Mixer using a mixing speed of 60 rpm. The carbon black (CB) was a commercial N339 grade from Columbian Chemicals. The initial mixer wall temperature was 110 °C, and the batch reached a temperature of ~150 °C when the 60 g batch was stopped after a mixing time of 5 min. In select cases, dilauroyl peroxide was incorporated into the carbon black-filled PB and into neat PB at levels of 0.2 and 2 wt % (relative to polymer). This peroxide was added by mixing on a two-roll mill at 60 °C.

A TA Instruments ARES (with dual 200 and 2000 g-cm force rebalance transducers) was used to make oscillatory shear measurements as a function of temperature. This testing employed a strain amplitude (γ) of 0.1%, a frequency of 0.5 Hz, and a parallel plate geometry with 10 mm diameter and 3 mm gap. The temperature was incrementally changed from −90 to 110 °C and

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*Corresponding author. E-mail: robertsonchris@bfusa.com.

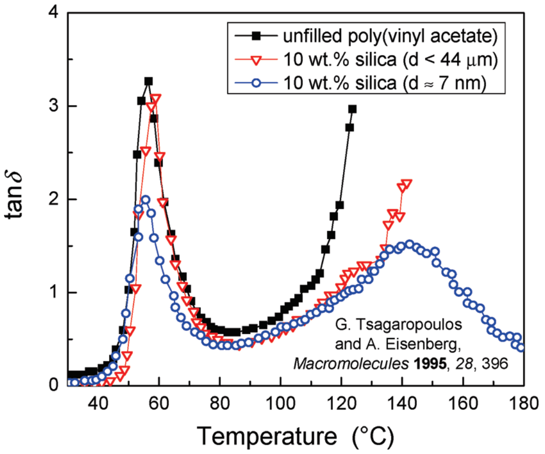

Figure 1. Mechanical loss tangent for poly(vinyl acetate), neat and filled with silica particles of the indicated size. Data are digitized and replotted from paper by Tsagaropoulos and Eisenberg.[11]

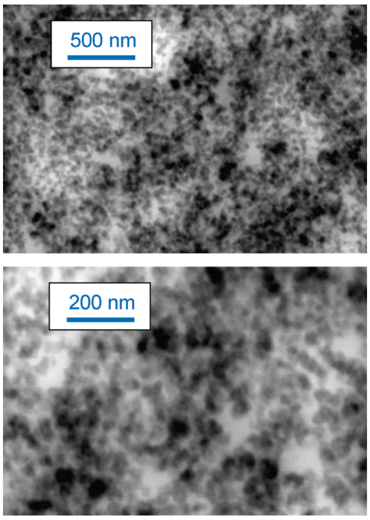

Figure 2. TEM images of N339 carbon black filled polybutadiene (ϕ = 0.23).

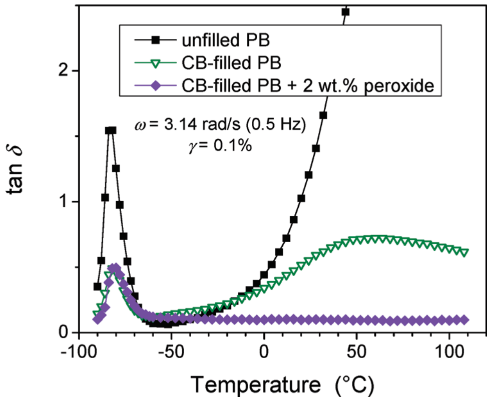

Figure 3. Effect of N339 carbon black filler (ϕ = 0.23), with and without cross-linking, on the loss tangent versus temperature response of polybutadiene.

equilibrated at each temperature before viscoelastic testing unlike the more usual nonisothermal temperature ramp experiment. An annealing period of 10 min at 150 °C was applied to the material between the parallel plates, and a small normal force of 10 g was maintained as the sample was then cooled to the starting temperature of −90 °C. This high-temperature annealing was sufficient to allow cross-linking to occur in the compounds that contained peroxide.

Modulated differential scanning calorimetry was performed using a TA Instruments modulated DSC (model 2920). After cooling to −120 at 5 °C/min, the samples (5−8 mg) were tested using an underlying heating rate of 5 °C/min with a superimposed temperature modulation having an amplitude of 0.5 °C and a period of 40 s. Prior to these measurements, a sapphire sample was used to calibrate the heat capacity signal of the instrument.

Transmission electron microscopy (TEM) was performed on cryogenically microtomed sections of the filled polymer compounds using a Philips CM12 instrument. Bound polymer was determined as the amount of polymer in the CB-filled polybutadiene which was not extracted after immersion of the sample in toluene solvent for 3 days at room temperature.

Results and Discussion

Representative findings from the investigations of Tsagaropoulos and Eisenberg are illustrated in Figure 1. Polymers containing small diameter ($d \approx 7$ nm) silica particles exhibited a tan δ peak at temperatures well above the peak associated with the glass transition of the polymer while large particles ($d \leq 45$ μm) did not produce the same peak. Tsagaropoulos and Eisenberg offered the explanation that this peak, which was 60−100 °C above the usual glass-to-rubber tan δ peak of the polymer, was the glass transition of severely mobility-restricted polymer chains near the particles. All of the various un-cross-linked polymers they studied showed this behavior. They published a communication[11] and a full paper[12] on this research, and together these papers have been cited more than 250 times.

To study further this influence of small, rigid particles on the segmental relaxation response of polymers, we reinforce polybutadiene (PB) with traditional carbon black at a filler volume fraction (ϕ) equal to 0.23. In particular, we use N339 carbon black (CB), although we have recorded similar responses from other polymers and other fillers. The average diameter of the primary particle of N339 CB is 26 nm, and the average diameter of fused aggregates is 75 nm. The reported filler surface area is 96 m^2/g.[18] Very good dispersion of the CB within the polybutadiene was verified using transmission electron microscopy (TEM), and representative TEM images are shown in Figure 2.

The effect of carbon black on small-strain dynamic mechanical viscoelastic behavior of polybutadiene was evaluated using oscillatory shear testing, and the loss tangent versus temperature responses are shown in Figure 3. Upon addition of filler, there is a reduction in the magnitude of the peak in tan δ corresponding to the usual glass transition of the polymer; this is due to the particle-induced reinforcement in the rubbery region above T_g which was demonstrated in previous work.[6] The unfilled PB exhibits terminal flow, with tan δ diverging toward infinity as temperature is increased. In contrast, the CB-filled PB displays a peak in tan δ in the higher temperature region. This tan δ peak for the particle-reinforced PB is about 130 °C above the main glass-to-rubber softening transition of the polymer and is very similar to the observations of Tsagaropoulos and Eisenberg (Figure 1). The location of this loss tangent dispersion for filled PB coincides with the terminal relaxation regime of the neat PB which suggests that this behavior may be related to chain diffusion/reptation. To clarify the situation, we also investigated CB-filled PB which was cross-linked with peroxide to remove any possibility of high-temperature relaxation due to disentanglement flow. The higher temperature peak disappears upon cross-linking the filled PB (Figure 3) which confirms that the origin of the peak in the un-cross-linked CB-reinforced PB is flow related and not due to a distinct, much higher temperature glass transition of polymer near the particles.

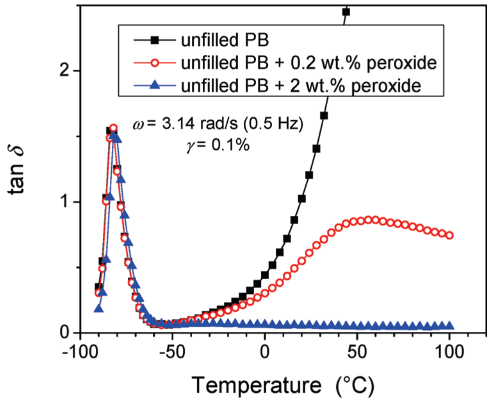

Figure 4. Effect of cross-linking on the loss tangent versus temperature response of polybutadiene.

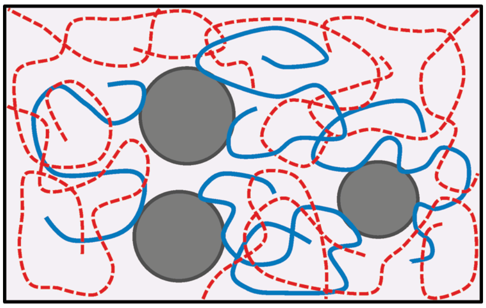

Figure 5. Schematic of polymer flow restriction due to particles. The solid blue chains have localized regions that are strongly adsorbed onto the filler particle surfaces which restrict the overall chain motion and inhibits flow relaxation. The dashed red chains are unattached and are free to flow/reptate. The consequence of this incomplete flow is a local peak in tan δ rather than the usual divergence of the loss tangent to infinity which is observed for unfilled polymers as temperature is increased (or frequency is decreased).

Even without particles, a similar tan δ peak can be produced via partial cross-linking of the polybutadiene. Incorporation of 0.2 wt % dilauroyl peroxide results in incomplete network formation in the unfilled PB, and the unattached chains can still undergo chain diffusion, leading to a higher temperature loss tangent peak (Figure 4). A fully developed cross-link network is formed at a peroxide level of 2 wt %, and the tan δ peak is not evident in this material. Adsorption of segments of polymer chains onto filler surfaces prevents the flow of those chains in a manner comparable to cross-linking. However, not all chains are attached to particles, and these unaffected chains are still free to undergo chain diffusion and flow. This incomplete chain relaxation leads to a loss tangent peak instead of the divergence of tan δ to infinity which occurs when the whole sample can experience disentanglement flow as temperature is increased (or frequency is decreased). A schematic of this polymer flow restriction due to particles is illustrated in Figure 5.

A close look at other existing literature concerning relaxation of nanoparticle–polymer composites confirms our findings. Zhu et al.[19] investigated the viscoelastic behavior of polybutadiene filled with silica particles. As this filled material approaches lower frequencies (higher temperatures), a terminal relaxation peak in the dynamic loss modulus (G'') is apparent in approximately the same location as the terminal G'' peak for the unfilled polymer (Figure 6). As frequency is reduced further, full terminal relaxation of the polymer in the filled material is prevented and the overall flow is arrested, with the storage modulus (G') remaining greater than G''. We determined tan δ from their reported G' and G'', and the results show a peak in tan δ in the lower frequency regime corresponding to the incomplete terminal relaxation (Figure 6).

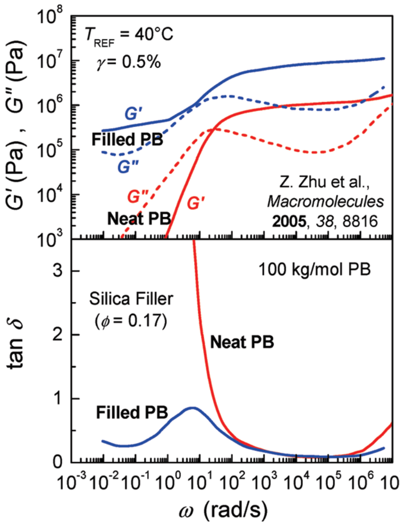

Figure 6. Viscoelastic master curves from approximate temperature–frequency superposition for polybutadiene (PB) and PB filled with silica particles. The upper plot represents data digitized and replotted from publication by Zhu et al.,[19] and the lower plot shows the tan δ calculated from their results (not shown in original publication).

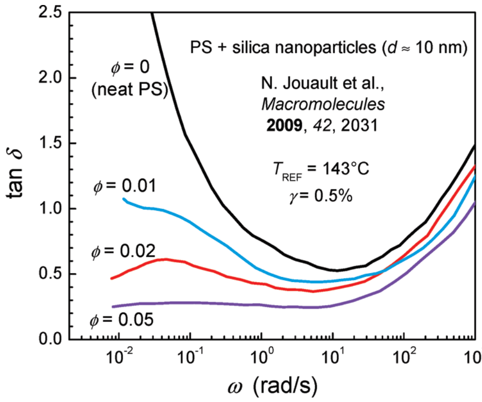

Figure 7. Viscoelastic tan δ master curves from approximate temperature–frequency superposition for polystyrene (PS) and PS filled with silica particles. Storage and loss moduli data were digitized from Jouault et al.[20] and used to calculate tan δ (not shown in original publication).

Viscoelastic analysis of polystyrene with added silica nanoparticles was recently reported by Jouault et al.[20] Increasing the volume fraction of the 10 nm diameter particles resulted in a systematic reduction in the extent of terminal relaxation flow (Figure 7). The incomplete disentanglement flow at $\phi = 0.02$ produces a localized peak in tan δ comparable to the behavior observed in our viscoelastic data and in the results of Zhu et al.[19] and Tsagaropoulos and Eisenberg.[11,12] It is quite remarkable that only a small amount ($\phi = 0.05$) of well-dispersed, nanosized particles is sufficient to completely immobilize the chain relaxation for the polystyrene at small dynamic strains, akin to fully cross-linking the polymer. High particle surface area, attractive interactions between polymer and filler, and small interparticle spacing are key to developing enough local sites of adsorption along a polymer chain to prevent chain diffusion and flow. This is why the polymer flow restraint effect was not noted for the micrometer-sized filler particles in the original work of Tsagaropoulos and Eisenberg.

Differential scanning calorimetry reveals that the carbon black particles have only a small impact on the polybutadiene glass transition (Figure 8). Even after solvent extraction of the polymer which is not interacting strongly with the filler in the CB-filled PB,

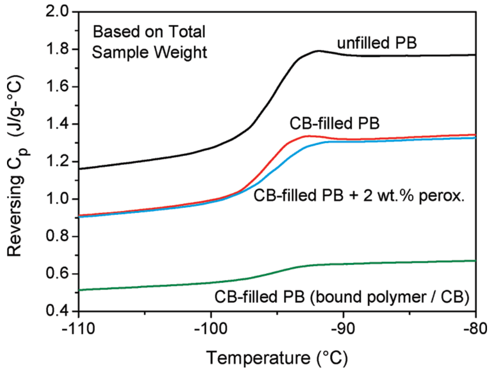

Figure 8. Modulated DSC results for the unfilled and filled PB materials. For the bound polymer/CB sample, 27.4% of the polybutadiene remained with the CB after 3 days of toluene extraction at room temperature.

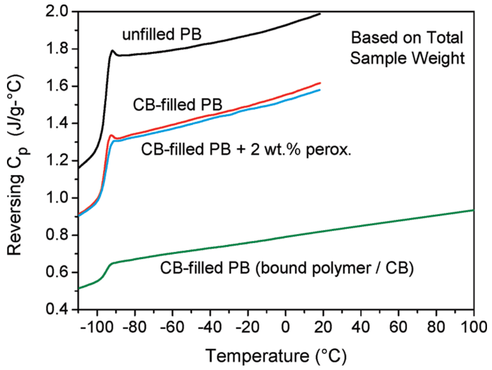

Figure 9. Modulated DSC results for the unfilled and filled PB materials for temperatures up to 100 °C. For the bound polymer/CB sample, 27.4% of the polybutadiene remained with the CB after 3 days of toluene extraction at room temperature.

Table 1. Results from Modulated Differential Scanning Calorimetry

	T_g (°C)	ΔC_p (J/(g °C)) [total weight]	ΔC_p (J/(g °C)) [polymer weight]
unfilled PB	−95.5	0.494	0.494
CB-filled PB	−95.3	0.314	0.502
CB-filled PB + 2 wt % peroxide	−94.4	0.313	0.501
CB-filled PB (bound polymer/CB)[a]	−94.7	0.085	0.497

[a] After 3 days extraction of CB-filled PB in toluene at room temperature, 27.4% of the PB remained with the CB.

there is no sign of any higher temperature glass transition (Figure 9), and an increase of only about 1 °C is noted in the main glass transition compared to the unfilled PB (Table 1). Furthermore, all of the polymer in the particle-containing samples is accounted for in the calorimetric response corresponding to the main glass transition (Table 1). The jump in heat capacity (ΔC_p) in the usual PB glass transition region is essentially identical for all of the samples based on the weight of polymer. For the materials we studied, there is no support from either dynamic mechanical analysis or differential scanning calorimetry that the glass transition/segmental relaxation is substantially modified due to the presence of particles.

Final Comments

We previously suggested[6] that the second tan δ peak noted in the work of Tsagaropoulos and Eisenberg was possibly related to a chain flow phenomenon rather than being associated with glass transition of the polymer proximate to the filler surfaces. This alternative explanation was developed by recognizing the presence of a similar local peak in tan δ in the flow region which is observed in sparsely branched polymers and bidisperse polymer blends[21−23] as well as in cross-linked polymer networks containing unattached chains.[24−26] Salaniwal, Kumar, and Douglas[27] proposed that the higher temperature loss tangent peak observed by Tsagaropoulos and Eisenberg may be due to polymer−filler "gel" with long structural lifetime. Their interpretation also attributes the relaxation response to longer-range flow behavior instead of local segmental dynamics. Our measurements on CB-reinforced polybutadiene, along with our analysis of literature data from Zhu et al.[19] for polybutadiene−silica materials and from Jouault et al.[20] for polystyrene filled with silica nanoparticles, provide the first solid evidence that the higher temperature tan δ peak in polymer−particle composites is not the glass transition response of an immobilized polymer shell but rather is associated with the suppression of flow relaxation (chain diffusion/reptation) of polymer chains due to interaction with the particles.

A slight shift and broadening of the glass transition of polymers, as induced by small particles, is a reasonable physical expectation, and the nature of the interfacial interactions between polymer and nanofiller appears to dictate whether a reduction, increase, or no change in T_g is produced when particles are introduced into polymers.[14,28,29] Generally, these T_g shifts are less than 10 °C even for high concentrations of well-dispersed nanoparticles.[2,10] The chain segments directly bonded/adsorbed onto the filler surface are immobilized and can function to limit the translational motion of the whole chain and prevent its disentanglement flow. However, a large fraction of directly bonded segments would be necessary to obtain an immobilized phase with a distinct T_g at much higher temperatures compared to the neat polymer. Such a high degree of polymer−filler bonding would impose severe entropic constraints on the chains and is hence an unfavorable and unlikely outcome. The research of Tsagaropoulos and Eisenberg[11,12] cannot be cited as evidence of severely retarded segmental motion of polymers due to nanosized particles, given the findings of our study. We hope that our present paper will prevent future misinterpretations of viscoelastic response in nanoparticle-filled polymers, such as is evident in recent publications.[30,31]

Acknowledgment. We thank Bridgestone Corporation for approving the publication of this research. Useful discussions with Prof. Sanat Kumar and Dr. Xiaorong Wang are gratefully acknowledged.

References and Notes

(1) Alcoutlabi, M.; McKenna, G. B. *J. Phys.: Condens. Matter* **2005**, *17*, R461.

(2) Robertson, C. G.; Roland, C. M. *Rubber Chem. Technol.* **2008**, *81*, 506.

(3) Sills, S.; Overney, R. M. In *Applied Scanning Probe Methods III*; Bhushan, B., Fuchs, H., Eds.; Springer-Verlag: Heidelberg, Germany, 2006; pp 83−130.

(4) Vieweg, S.; Unger, R.; Heinrich, G.; Donth, E. *J. Appl. Polym. Sci.* **1999**, *73*, 495.

(5) Rodriguez, J. G. I.; Carreira, P.; Garcia-Diez, A.; Hui, D.; Artiaga, R.; Liz-Marzan, L. M. *J. Therm. Anal. Calorim.* **2007**, *87*, 45.

(6) Robertson, C. G.; Lin, C. J.; Rackaitis, M.; Roland, C. M. *Macromolecules* **2008**, *41*, 2727.

(7) Bogoslovov, R. B.; Roland, C. M.; Ellis, A. R.; Randall, A. M.; Robertson, C. G. *Macromolecules* **2008**, *41*, 1289.

(8) Fritzsche, J.; Klüppel, M.; Meier, J. G. *Kautsch. Gummi Kunstst.* **2009**, *62*, 319.

(9) Kraus, G.; Gruver, J. T. *J. Polym. Sci., Part A-2: Polym. Phys.* **1970**, *8*, 571.

(10) Harton, S. E.; Kumar, S. K.; Yang, H.; Koga, T.; Hicks, K.; Lee, H. K.; Mijovic, J.; Liu, M.; Vallery, R. S.; Gidley, D. W. *Macromolecules* **2010**, *43*, 3415.

(11) Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* **1995**, *28*, 396.

(12) Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* **1995**, *28*, 6067.

(13) Arrighi, V.; McEwen, I. J.; Qian, H.; Serrano Prieto, M. B. *Polymer* **2003**, *44*, 6259.

(14) Bansai, A.; Yang, H. C.; Li, C. Z.; Benicewicz, R. C.; Kumar, S. K.; Schadler, L. S. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2944.

(15) Oh, H.; Green, P. F. *Nature Mater.* **2009**, *8*, 139.

(16) Fragiadakis, D.; Pissis, P.; Bokobza, L. *Polymer* **2005**, *46*, 6001.

(17) Gagliardi, S.; Arrighi, V.; Ferguson, R.; Telling, M. T. F. *Physica B: Condens. Matter* **2001**, *301*, 110.

(18) Hess, W. M.; McDonald, G. C. *Rubber Chem. Technol.* **1983**, *56*, 892.

(19) Zhu, Z.; Thompson, T.; Wang, S.-Q.; von Meerwall, E. D.; Halasa, A. *Macromolecules* **2005**, *38*, 8816.

(20) Jouault, N.; Vallat, P.; Dalmas, F.; Said, S.; Jestin, J.; Boue, F. *Macromolecules* **2009**, *42*, 2031.

(21) Robertson, C. G.; Garcia-Franco, C. A.; Srinivas, S. *J. Polym. Sci., Polym. Phys.* **2004**, *42*, 1671.

(22) Struglinski, M. J.; Graessley, W. W. *Macromolecules* **1985**, *18*, 2630.

(23) Kasehagen, L. J.; Macosko, C. W.; Trowbridge, D.; Magnus, F. *J. Rheol.* **1996**, *40*, 689.

(24) Urayama, K.; Yokoyama, K.; Kohjiya, S. *Macromolecules* **2001**, *34*, 4513.

(25) Ndoni, S.; Vorup, A.; Kramer, O. *Macromolecules* **1998**, *31*, 3353.

(26) Kramer, O.; Greco, R.; Neira, R. A.; Ferry, J. D. *J. Polym. Sci., Polym. Phys.* **1974**, *12*, 2361.

(27) Salaniwal, S.; Kumar, S. K.; Douglas, J. F. *Phys. Rev. Lett.* **2002**, *89*, 258301.

(28) Rittigstein, P.; Torkelson, J. M. *J. Polym. Sci., Polym. Phys.* **2006**, *44*, 2935.

(29) Lee, K. J.; Lee, D. K.; Kim, Y. W.; Choe, W. S.; Kim, J. H. *J. Polym. Sci., Polym. Phys.* **2007**, *45*, 2232.

(30) Chen, L.; Zheng, K.; Tian, X. Y.; Hu, K.; Wang, R. X.; Liu, C.; Li, Y.; Ciu, P. *Macromolecules* **2010**, *43*, 1076.

(31) Comer, A. C.; Heilman, A. L.; Kalika, D. S. *Polymer* **2010**, *51*, 5245.