Rheology of a Miscible Blend of SAN and SMA

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ABSTRACT: We present results of oscillatory shear rheology experiments on miscible blends of commercial styrene-acrylonitrile (SAN) and styrene-maleic anhydride (SMA) copolymers. We find that this blend system upholds the empirical time-temperature superposition principle. We compare the thermorheological behavior in this system with other blends, on which oscillatory shear data have been published in the literature. We show that thermorheological behavior in these blends is indeed comparable to other known thermorheologically simple blends. Thermorheological simplicity in this blend is nicely anticipated by a thermorheological phase diagram in the parameter space of dynamic asymmetry and free volume, which we have recently proposed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1245–1249, 2000

Key words: miscible polymer blends; rheology; time-temperature superposition; thermorheological simplicity; free volume

INTRODUCTION

We present oscillatory shear rheology data on a miscible blend of two copolymers: styrene-acrylonitrile (SAN) and styrene-maleic anhydride (SMA). Many workers have employed different techniques such as calorimetry, Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), and positron annihilation lifetime spectroscopy (PALS) to study miscibility in this blend system.[1–4] It is well accepted that the two copolymers are melt miscible. In this note, we show that despite strong dynamic asymmetry ($T_g^{\mathrm{SMA}} - T_g^{\mathrm{SAN}} = 47$ K), this system follows the time-temperature superposition (tTS) principle[5] nearly as well as typical homopolymers, as judged from the shift in the loss tangent minimum with temperature (in the rubbery plateau). Thermorheological simplicity in this system is indeed well anticipated by an empirical thermorheological "phase diagram" which we have recently proposed.[6]

EXPERIMENTAL

The SMA used in this study was produced by DSM (Geleen, Netherlands). The SAN was obtained from BASF. The SAN ("Luran 2770"; 27% AN) had $M_w = 70\ 000$ and $M_w/M_n = 2.0$. The SMA ("Stapron S"; 28% MA) had $M_w = 110\ 000$ and $M_w/M_n = 2.5$. The T_g of pure SAN is 106°C, that of pure SMA is 153°C, measured using DMA in torsion at a frequency of 0.2 Hz. Blends were prepared in the melt state using a Schwabenthan single screw extruder operated at 230–250°C, with a throughput of 8–10 kg/hour. The compositions of blends studied were 20, 40, 60, and 80% SMA (by weight). From DMA, the blends show single T_gs of 137, 127, 118, and 111°C, respectively. We take this as necessary evidence for miscibility in the blends.

Oscillatory shear experiments were performed at DSM on a Rheometrics 605 rheometer. The

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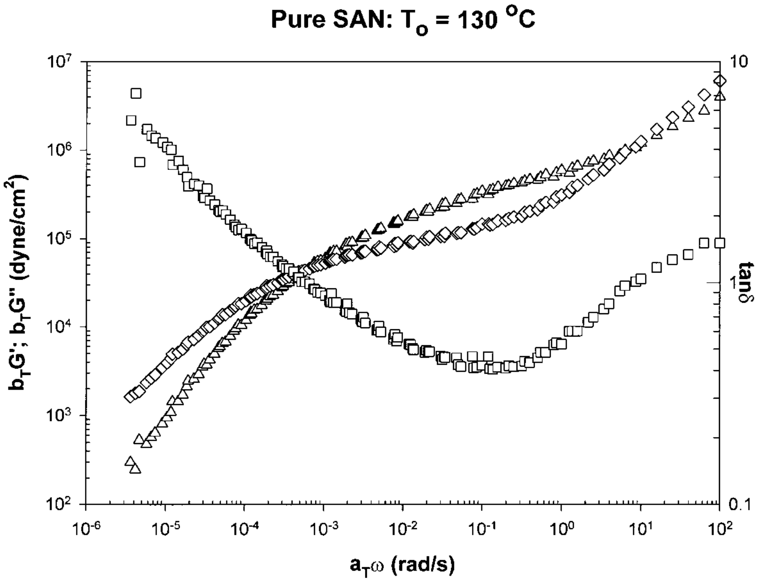
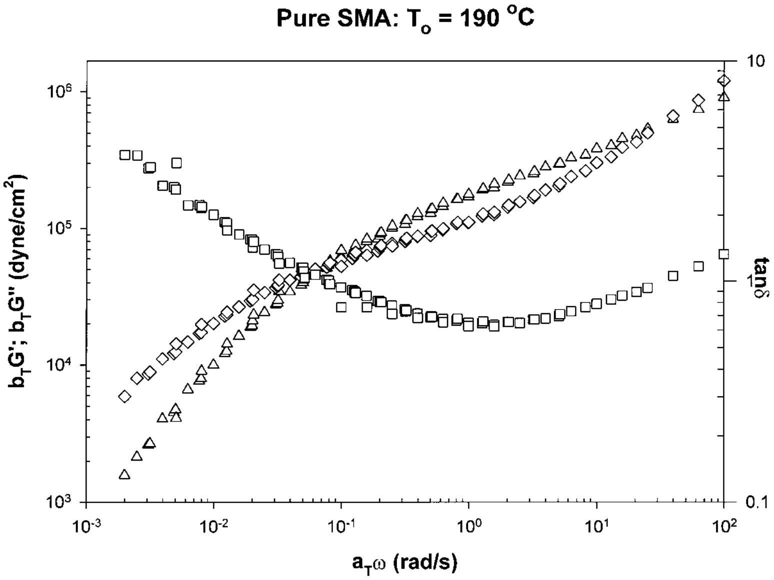


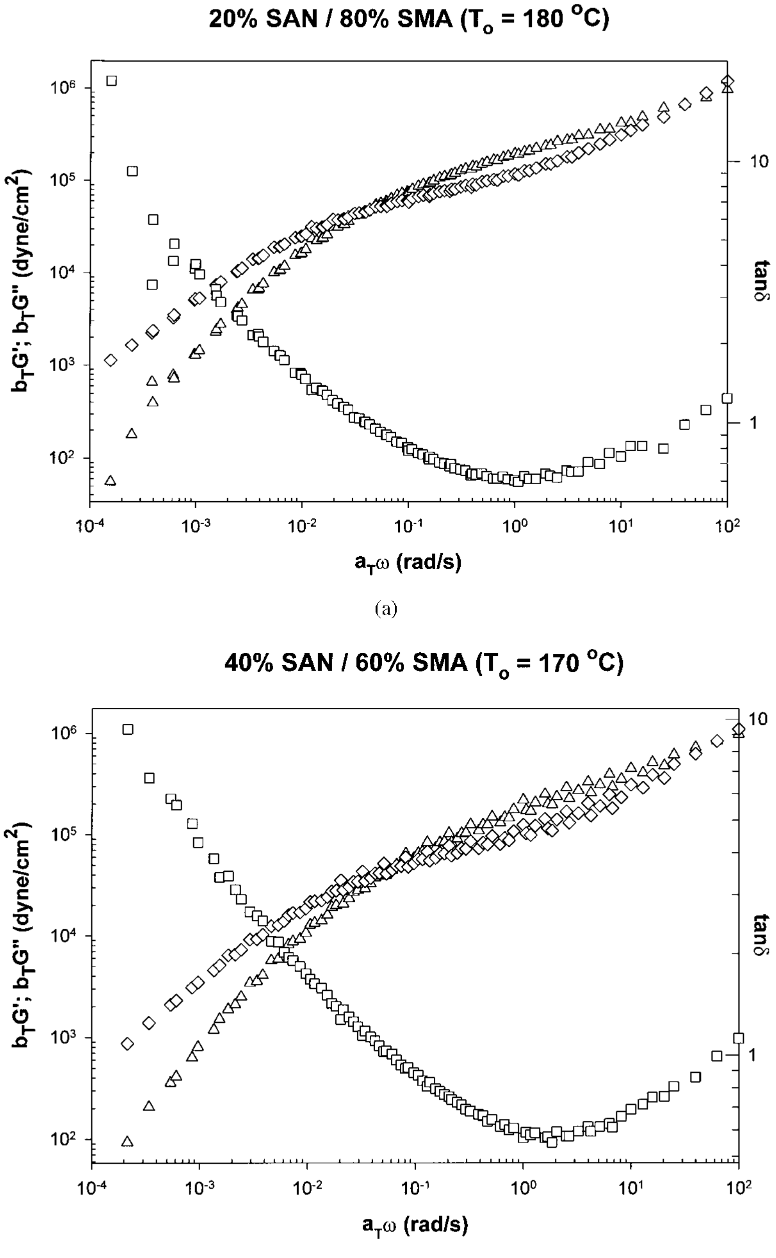
(a)



(b)

Figure 1 Master curves of oscillatory shear data for pure components: (a) pure SAN, referenced to 130°C (T_g + 24 K), using data at 130, 140, 150, 160, 170, 180, 190, 200, and 210°C, and, (b) pure SMA, referenced to 190°C (T_g + 37 K), using data at 190, 200, 210, 220, 230, and 240°C.

applied strain amplitudes were always less than the maximum strain for linear response, as determined from strain sweeps at each temperature. Twenty-five-mm diameter plates were used. The polymer samples were prepared by compression molding above T_g in a table press. Temperature control was maintained by a steady flow of nitrogen gas through the sample chamber. Frequencies between 10^2 and 10^{-1} rad/s were typically used in the oscillatory shear experiments. The linear viscoelasticity of pure SAN and pure SMA were studied between 130°C and 210°C, and 190°C and 260°C, respectively. The viscoelasticity of blends was studied at temperatures in between 160°C and 230°C. Temperature increments of 10 K were used in all cases.



(a)

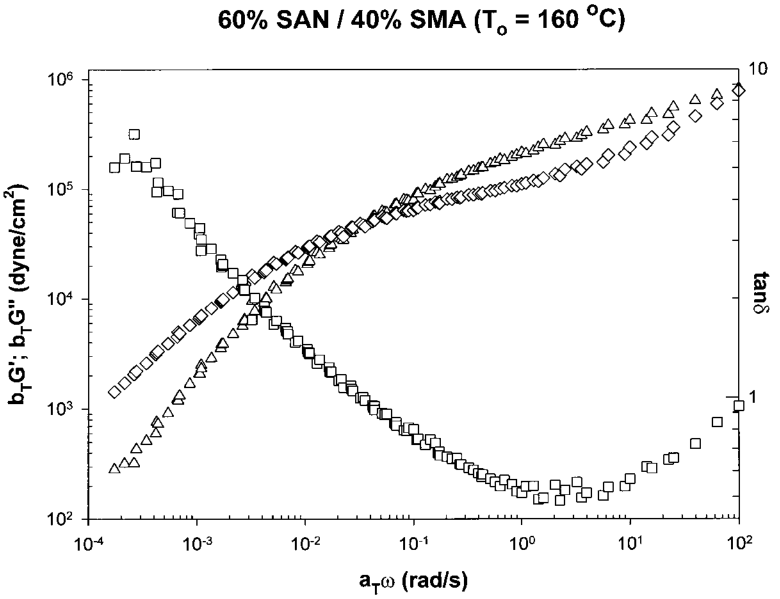
(b)

Figure 2 Master curves of oscillatory shear data for the blends: (a) SAN/SMA 20/80 blend, referenced to 180°C (T_g + 43 K), using data at 180, 190, 200, 210, 220, and 230°C, (b) SAN/SMA 40/60 blend, referenced to 170°C (T_g + 43 K), using data at 170, 180, 190, 200, 210, and 220°C, (c) SAN/SMA 60/40 blend, referenced to 160°C (T_g + 42 K), using data at 160, 170, 180, 190, 200, 210, 220, and 230°C, and (d) SAN/SMA 80/20 blend referenced to 160°C (T_g + 49 K), using data at 160, 170, 180, 190, 200, 210, and 220°C.

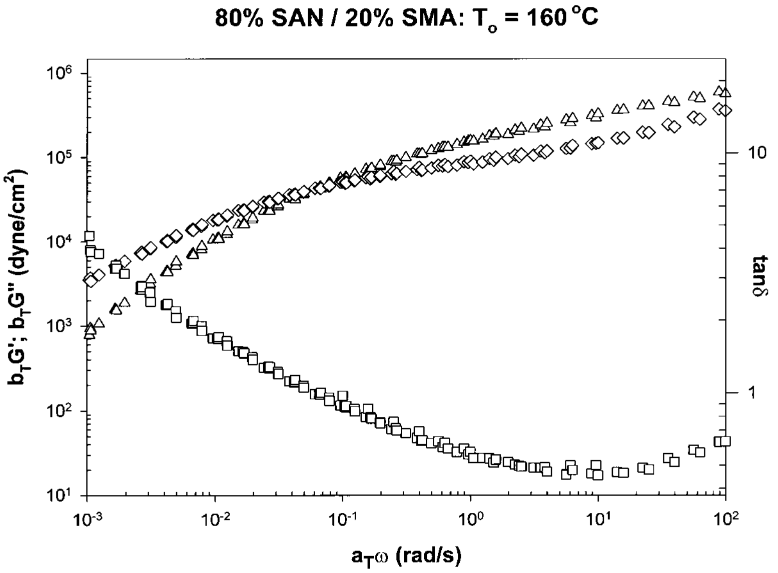
RESULTS AND DISCUSSION

The tTS principle[5] gives a relation for the frequency ω dependence of the complex modulus G^* at any temperature T to that at a reference temperature T_0.

$$G^*(\omega, T) = b_T G^*(a_T\omega;\ T_0) \tag{1}$$



(c)



(d)

Figure 2 (*Continued from previous page*)

The frequency dependence of all data at temperature T is thus related with data at the reference temperature T_0 by means of a frequency-scale shift factor a_T and a modulus-scale shift factor b_T. Time-temperature superposition was applied to each of the pure components, and master curves were prepared according to this principle. The master curve for pure SAN and pure SMA are shown in Figures 1a and 1b, respectively. Our materials show small modulus-scale shifts ($b_T \cong 1$), and we shall not discuss them here. The frequency-scale shifts are significant, and they exhibit classical Williams–Landel–Ferry (WLF)[7] temperature dependence. Time-temperature superposition was also applied to the blends. The master curves of the 20, 40, 60, and 80% SAN blends are shown in Figures 2a, 2b, 2c, and 2d, respectively. We have extensively used the loss tangent (tan $\delta = G''/G'$), to ensure that the vertical scale shifts do not allow false superposition. The frequency-scale shift factors were determined by first shifting tan δ curves, and then the mod-

Table I Comparison of the Derivative $d \tan \delta_{min}/dT$ (a Measure of the Effectiveness of tTS) for Pure SAN, Pure SMA, and the SAN/SMA Blends

System	$\|d \tan \delta_{min}/dT\|$
SAN	5.8×10^{-4}
20% SAN/80% SMA	3.4×10^{-4}
40% SAN/60% SMA	7.1×10^{-4}
60% SAN/40% SMA	7.0×10^{-4}
80% SAN/20% SMA	1.4×10^{-3}
SMA	3.4×10^{-4}
PEO/PMMA	$\sim 2 \times 10^{-3}$
PS/PVME	$\sim 1 \times 10^{-3}$
PI/PVE	$\sim 1 \times 10^{-3}$
1,2-PB/1,4-PB	$\sim 3 \times 10^{-3}$

For comparison, values of $d \tan \delta_{min}/dT$ for thermorheologically complex blends (PEO/PMMA, PS/PVME, PI/PVE, and 1,2-PB/1,4-PB; see [6] for details) are also provided.

ulus-scale shift factors were independently determined from modulus-scale shifts of $G^*(a_T\omega; T_0)$. Figures 1 and 2 demonstrate that tTS holds not only in the pure components, but also in the blends. Next, we shall make a quantitative comparison of the effectiveness of tTS in pure SAN, pure SMA, and SAN/SMA blends, and also compare the behavior of these blends to other miscible blends.

To quantitatively compare the efficacy of tTS in these systems, we determine the temperature dependence of the minimum in tan δ (henceforth denoted as tan δ_{min}) at the high frequency end of the rubbery plateau, which is a convenient and well-defined point. Moreover, reproducibility in tan δ is much greater than that in G' and G''. Table I shows the value of $|d \tan \delta_{min}/dT|$ for the pure components and the blends. For most of the SAN/SMA blends, the value of this derivative is only marginally higher than that in pure SAN and pure SMA. Moreover, the value of $|d \tan \delta_{min}/dT|$ in SAN/SMA blends is significantly smaller than in other miscible blend systems that are known to exhibit thermorheological complexity.[6] We cite these for comparison, and to produce as evidence of thermorheological simplicity in the SAN/SMA blend system.

We do wish to point out that both the SAN and SMA used in this study are very polydisperse commercial materials, and we can not rule out the role of polydispersity in bringing about the observed thermorheological simplicity. We also emphasize that in the absence of oscillatory shear data near the glass transition, we are also unable to make any statement about the validity of tTS across the entire viscoelastic spectrum. However, in the rubbery plateau region, tTS works nearly as well in SAN/SMA blends as it does in its constituent copolymers, and indeed in many other homopolymer melts.[6]

We present these experimental data in order to stimulate interest in the study of blends such as SAN/SMA, which, according to some workers,[1] exhibits strong exothermic interactions. A comprehensive study of the thermodynamics of this blend (using small-angle neutron scattering) and rheology (using fractionated, and thus, less polydisperse materials) will help us get a clearer picture of the statics and dynamics of this blend system. It will improve our understanding of the interplay between the statics and dynamics of such systems, which may fall in the class of strongly interacting miscible blends.

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REFERENCES

1. Kim, J. H.; Barlow, J. W.; Paul, D. R. J Polym Sci Pt B: Polym Phys 1989, 27, 223.
2. Heinen, W.; Wenzel, C. B.; Rosenmoeller, C. H.; Mulder, F. M.; Boender, G. J.; Lugtenburg, J.; de Groot, H. J. M.; van Duin, M.; Klumpermann, B. Macromolecules 1998, 31, 7404.
3. Heinen, W. Grafting of Polyolefins and Miscibility in Copolymer Mixtures—Studies of Polymers on the Atomic Level with Site-Specific Isotope Enrichment and NMR. Ph.D. Thesis, Leiden University, Leiden, 1996.
4. Wästlund, C.; Berndtsson, H.; Maurer, F. H. J. Macromolecules 1998, 31, 3322.
5. Ferry, J. D. Viscoelastic Properties of Polymers, 3rd Ed.; Wiley: New York, 1980.
6. Pathak, J. A.; Colby, R. H.; Kamath, S. Y.; Kumar, S. K.; Stadler, R. Macromolecules 1998, 31, 8988.
7. Williams, M. L.; Landel, R. F.; Ferry, J. D. J Am Chem Soc 1955, 77, 3701.