# Vibration Damping and Electrical Conductivity of Styrene–Butyl Acrylate Random Copolymers Filled with Carbon Black

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**ABSTRACT:** Emulsion-polymerized poly(styrene-*rand*-butyl acrylate) (St–BA) copolymers exhibit damping capabilities over a wide temperature range with changes in the monomer ratio. Blending copolymers of different compositions results in a multidamping peak, further widening the effective damping temperature range. Adding carbon black (CB) reduces the peak damping intensity but enhances damping at higher temperatures. The addition of dodecyl benzene sulfonic acid to an St–BA/CB aqueous dispersion improves the dispersion of CB in the polymer, reducing the percolation threshold and improving the conductivity while slightly affecting the mechanical behavior. The electrical properties of the St–BA/CB system are affected by the copolymer composition, influencing the polymer surface tension. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1922–1928, 2010

**Key words:** glass transition; thermoplastics; viscoelastic properties

## INTRODUCTION

Most geometric structures, from the world's largest bridges and aircraft to the smallest printed circuits in a computer, experience vibratory motions. These undesired vibrations waste energy and create noise. Therefore, vibration control is an important engineering challenge. Passive damping is the main method for controlling the vibrations in a structure; it refers to a structure's ability to dampen its own oscillations. The damping of vibrations in metal sheets can be achieved through the construction of metal sheet laminates, which contain a core layer of a viscoelastic material and exhibit an energy loss within the desired temperature and frequency ranges. In certain applications, the laminates are required to also be electrically conductive.

Polymers, because of their viscoelastic properties, are generally suitable for vibration-damping applications. When polymers are externally vibrated at the proper temperature and frequency, molecular vibrational energy is converted into heat. Usually, homopolymers possess efficient damping in a temperature range of only 20–30°C around their glass-transition temperature $(T_g)$;[1] however, desired damping materials should exhibit a wider temperature range.[2] Using copolymerization is one of the conventional ways of broadening the $T_g$ range. The dynamic mechanical properties of random copolymers are strongly influenced by the characteristics of the monomers as well as the copolymer composition and its heterogeneity.[3,4]

The properties of filled polymers are determined by the properties of the components, the morphology of the system, the shape of the filler phase, and the nature of the polymer/filler interface. Rigid fillers make a polymer stiffer, and this is reflected in an increase in the storage modulus of the material and, in most cases, in a decrease in the damping. However, in some cases, the damping peak is increased with the addition of filler particles because of particle–particle or particle–polymer friction.[5,6] Fillers have a larger effect on the modulus above $T_g$ than below it because of the larger modulus ratio of the components when the polymer is in the rubbery state in comparison with the rigid filler.[7] If the polymer binds to the filler, the molecular motion of the polymer is restricted, and the $T_g$ value of the portion of the polymer in the vicinity of the filler may increase. This effect changes with the distance from the filler particle surface. The total effect is to broaden the transition and raise its peak temperature. The effect should increase with the filler content and surface area.[8] In the case of phase-separated

polymers, the filler may be located in either phase, in both, or at their interface.[9]

The electrical conductivity of polymer composites containing conductive fillers is based on the principles of percolation. Carbon black (CB) filled polymers have been extensively studied and used when moderate conductivity is required.[10,11] Recent studies have focused on reducing the CB content while maintaining relatively high conductivity, processability, and desired mechanical properties. This can be achieved in several ways, such as the addition of CB to immiscible polymer blends or two-phase block copolymers.[12,13] The preferential location of the CB within one of the phases or at their interface reduces the percolation content and increases the conductivity.[14,15] Another way of reducing the percolation threshold is blending the CB into an aqueous polymer latex.[16]

Grunlan and coworkers[17–19] compared the electrical conductivity of a CB-containing poly(vinyl acetate) latex and a poly(N-vinylpyrrolidone) aqueous solution as composite starting materials. A dramatic difference between the percolation threshold values was obtained: 2.5 vol % for the latex and 15 vol % for the latter. When polymer latex composites undergo drying, the CB particles are located in a nonrandom manner, creating a connected network at very low filler contents. During the composite latex drying period, a sample goes through the following sequence of stages. Initially, the water suspends the latex particles and the filler particles in a random arrangement. After water evaporation, the filler is forced into the interstitial spaces between the latex particles. Finally, the latex particles coalesce, forming a continuous phase, and this allows the conductive filler to percolate through the system.

The main goal of this research was to investigate the vibrational damping abilities and electrical conductivity of CB-filled poly(styrene-rand-butyl acrylate) (St–BA) copolymers. Furthermore, we sought ways to reduce the percolation threshold and increase the efficient damping temperature range.

## EXPERIMENTAL

St–BA copolymers, prepared by emulsion polymerization, were supplied by BG Polymers (Beit-Gouring, Israel) as emulsions containing 50 wt % solids. Four copolymers were used, differing in their styrene/butyl acrylate (BA) ratios (30/70, 50/50, 70/30, and 90/10).

The CB used in this project was Ketjenblack EC-600, an electrically conductive CB available from Akzo Noble, Inc. (Amsterdam, The Netherlands). The highly branched, high-surface-area CB structure allows it to form continuous networks, which result in enhanced electrical conductivity at low CB contents.

Before the polymer was blended with CB, the desired amount of CB was dispersed in water containing a small amount of a dispersant [dodecyl benzene sulfonic acid (DBSA)]. To well disperse the CB, ultrasonication was used. The so-prepared water/CB dispersion was added to a desired amount of the copolymer emulsion and then well blended. The emulsion was then destabilized, and the solids (copolymer/CB) were separated from the aqueous medium and dried in vacuo. The dry blends were compression-molded at 70–90°C, forming 3-mm-thick plaques. Samples were cut from the plaques for characterization.

To quantify the effect of DBSA on the dispersion of CB in water, a burette with a scale was used. First, water with different amounts of DBSA and CB was mixed with ultrasonication, and this resulted in homogeneous dispersions. Then, the mixtures were placed in the burette, and the height of the black color, indicating the stability of the dispersion, was followed.

Room-temperature direct-current resistance measurements were carried out. The conductivity was measured through the thickness for samples ($2 \times 2$ $cm^2$) cut from the compression-molded plaques. Silver paint was applied to minimize contact resistance between the sample and electrodes. The conductivity was measured with a Keithley Multimeter 2000 (Cleveland, OH); a constant direct-current voltage (10 V) was applied.

A Mettler–Toledo (Columbia, OH) DSC821 differential scanning calorimeter was employed to study the thermal behavior of all blends. Samples of approximately 6–9 mg were placed in a standard aluminum crucible and heated under an inert nitrogen atmosphere at a rate of 10°C/min from −100 to 150°C (first run) to erase the thermal history. The samples were then cooled and reheated (second run) at the same rate and in the same temperature range.

The blend's dynamic mechanical behavior in the bending-shear, single-cantilever mode was investigated with a Rheometrics MK3 dynamic mechanical thermal analyzer (Ithaca, NY). Samples ($3 \times 0.5 \times 0.3$ $cm^3$) were subjected to a sinusoidal bending strain at a frequency of 1 Hz while being heated at a rate of 3°C/min. The dynamic mechanical thermal analysis (DMTA) measurements provided the material's storage modulus, loss modulus, and internal friction [damping factor (tan δ)] as functions of the temperature and frequency.

## RESULTS AND DISCUSSION

The suitability of an St–BA copolymer containing CB as a vibration-damping material was studied through an examination of the electrical and dynamic mechanical properties of St–BA filled with

TABLE I
Normalized Black Height for Different Mixtures of Water, CB, and DBSA at Several Times

| CB content (%) | DBSA content (%) | Black height (normalized) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Initial | 15 min | 30 min | 45 min | 60 min | 75 min | 1 week |
| 0.13 | 0 | 1 | 0.47 | 0.38 | 0.35 | 0.32 | 0.32 | 0.29 |
| 0.25 | 0 | 1 | 0.94 | 0.82 | 0.78 | 0.75 | 0.72 | 0.63 |
| 0.13 | 0.1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 0.25 | 0.1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.95 |
| 0.13 | 0.2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 0.25 | 0.2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

The data for this table were taken from a private communication from M. Narkis that was based on a project carried out by R. Rahman, H. Shitrit, and Y. Saar (Department of Chemical Engineering, Technion) in 2007.

CB. The advantages of mixing the conducting particles with the polymer particles dispersed in an aqueous medium over mixing the conducting particles in the molten polymer matrix were examined.

The first step in the preparation of the St–BA/CB blends was to uniformly disperse the CB in the aqueous latex. Table I depicts the effect of the presence of DBSA on the CB dispersion in water. When the CB was dispersed in water without DBSA, sedimentation was observed after a very short time. The addition of DBSA to the water/CB dispersion clearly improved the homogeneity and stability of the dispersion; CB sedimentation was not observed even after a week. Slight instability appeared after a week in the samples with low DBSA contents and high CB contents. This improvement was observed also with the naked eye; the blend without DBSA appeared heterogeneous, containing relatively large black agglomerates, whereas the black blends with DBSA appeared homogeneous.

DBSA provided quite efficient breakup of the CB agglomerates during composite mixing. The effect of DBSA on conductivity was examined with the polymer containing 50% BA. The conductivity of the St–BA/CB blends was measured for blends with different CB/DBSA ratios (see Fig. 1). The percolation threshold was affected by the presence of the dispersant. In blends containing equal amounts of DBSA and CB, a drastic change in resistivity appeared with the lowest CB content. As the DBSA content decreased, the percolation threshold increased. The percolation threshold changed from about 1.2 to 2.2 phr CB for samples containing 1 : 1 CB/DBSA and no DBSA, respectively. The final resistivity was also influenced by DBSA, albeit to a lesser extent. The presence of DBSA reduced the resistivity at 6 phr CB, and as the DBSA content increased, the resistivity at 6 phr CB decreased. The sample containing 1 : 0.5 CB/DBSA exhibited unusual behavior: its resistivity at 6 phr CB was lower than that of the 1 : 1 CB: DBSA sample.

These results are in disagreement with the results of Grunlan et al.[20] They used poly(vinyl acetate)

latex as a matrix starting material and alkanol ammonium salt of a poly(carboxylic acid) as a dispersing aide added during composite mixing. They found that the percolation threshold increased and the final conductivity slightly decreased with an increasing amount of the dispersing agent. The researchers claimed that the reason for this behavior was the decrease in the CB aggregate size and the prevention of reagglomeration during drying. The dispersing agents used presently and by Grunlan et al. help to disperse CB particles in a similar manner; breaking up CB agglomerates and stabilizing their dispersion in water. There are two competing mechanisms with respect to the effect of a dispersant on conductivity. The good dispersion of CB particles in the initial stages of sample preparation promotes efficient conductive path creation and, therefore, is important for reducing the percolation threshold. On the other hand, the long dispersing agent molecules, adsorbed onto the CB particles, interfere with the electronic conductivity. The reason for the difference between the results obtained in the two studies could be the dispersant molecule length; DBSA has significantly
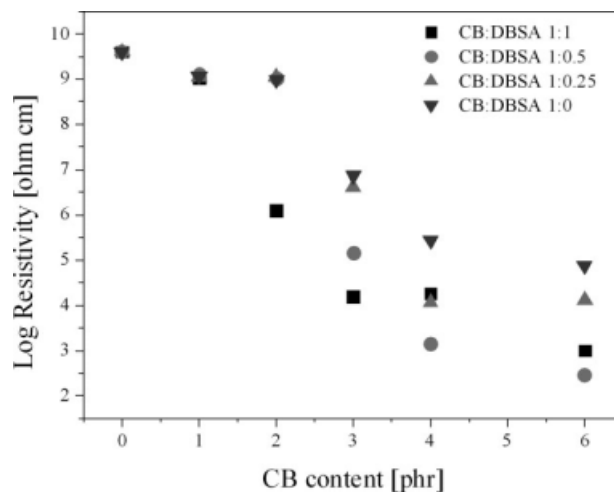


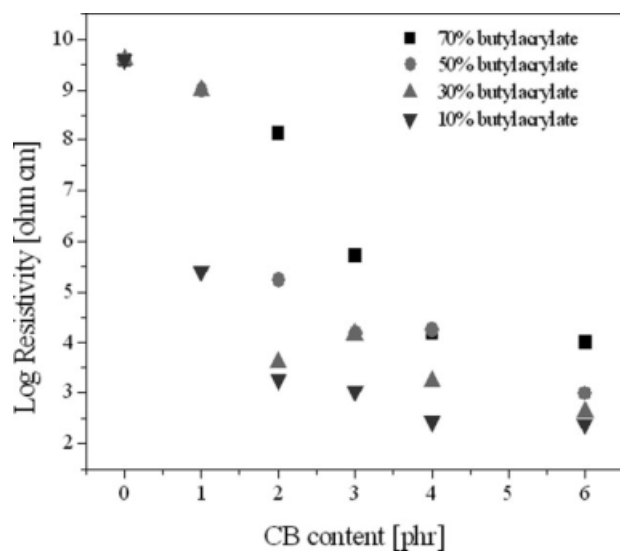**Figure 1** Effect of DBSA on the conductivity of the St–BA copolymer (50% BA).

**Figure 2** Effect of the St–BA composition on the conductivity (1 : 1 CB/DBSA).



**Figure 3** Effect of the PS content on the percolation threshold.

fewer carbon atoms in its backbone than the poly (carboxylic acid) salt. There might be an optimal number of backbone carbon atoms for a dispersant that minimizes its negative effect on conductivity.

The effect of the copolymer composition on conductivity was studied. Figure 2 shows a substantial effect of the composition on the percolation threshold and on the conductivity level. The copolymer containing 10% BA had the lowest percolation threshold (∼0.5 phr CB) and the lowest resistivity at 6 phr CB. As the content of BA in the copolymer increased, the percolation threshold increased, and the resistivity at 6 phr CB increased as well. This may have been a result of the surface properties of the CB and polymer. Better wetting of the CB by the polymer, due to similar surface tensions, could improve the CB dispersion within the matrix. Polystyrene (PS) has greater surface tension (39.3 dyn/cm) than poly(butyl acrylate) (33.7 dyn/cm). Figure 3 shows qualitatively the percolation threshold versus the copolymer composition. It is clear that as the PS content increased, the threshold decreased.

Dispersing the CB within a polymer latex resulted in systems with low percolation thresholds. The system based on the copolymer containing 10% BA exhibited a percolation threshold of just 0.5 phr CB. Blending the conducting CB particles with polymer emulsion particles decreased the resistivity of the polymer with a high BA content. The CB particles were located in the interstices between the polymer particles and created a stable continuous network.

Figure 4 depicts the $T_g$ values of copolymers (without CB) of various compositions as measured by differential scanning calorimetry (DSC) and DMTA (tan δ). A single glass transition was

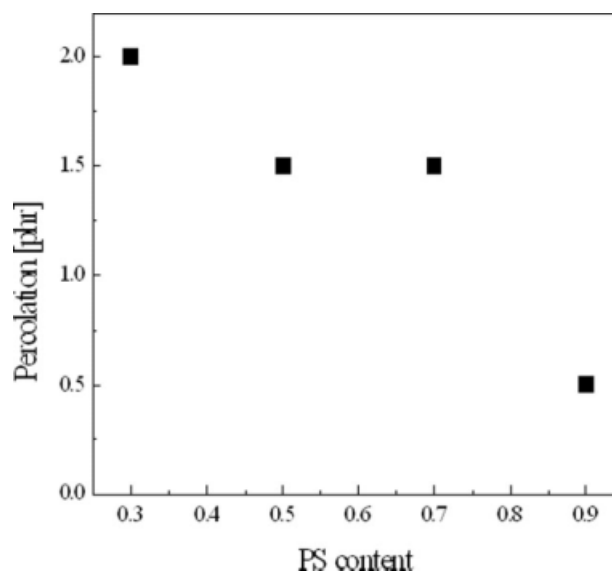detected; this is characteristic of random copolymers. The $T_g$ values of the copolymer were between those of the homopolymers as a function of the ratio of the two monomers, as expected for random copolymers. The $T_g$ values were compared to values calculated with the Fox equation. The $T_g$ values measured by DMTA were higher than the calculated ones. The deviation of the experimental values from the calculated ones increased with the BA content in the copolymer. The Fox equation calculates the $T_g$ values of random copolymers only by the proportion of the monomers in the polymerization; it does not consider the nature of the homopolymers and the
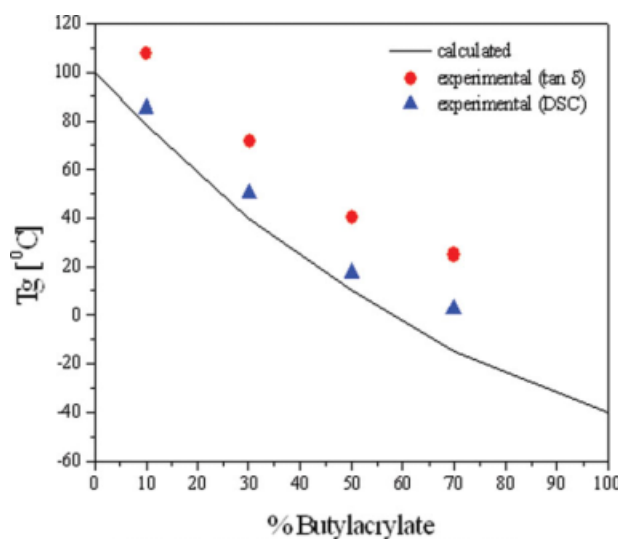


**Figure 4** Effect of the St–BA copolymer composition on $T_g$ as measured by DSC and DMTA (tan δ) and calculated with the Fox equation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

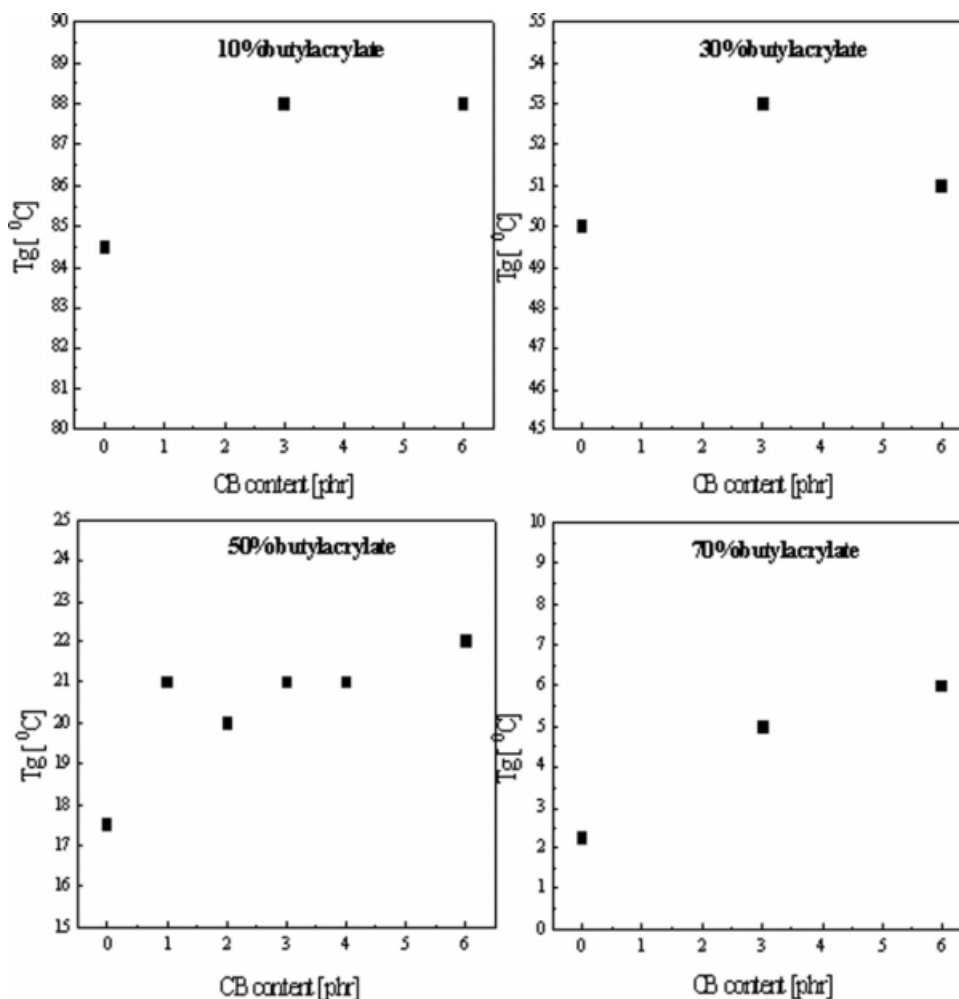**Figure 5** Influence of CB on the $T_g$ values of St–BA copolymers measured by DSC: (a) 10, (b) 30, (c) 50, and (d) 70% BA.

interaction between the components in the random copolymer. The $T_g$ values measured by DSC were in good agreement with the calculated ones, which were based on the $T_g$ values of the respective homopolymers. When comparing the DMTA and DSC $T_g$ values, we found that the transition temperature measured by DMTA was, as expected, always higher than the DSC $T_g$.

The presence of CB altered the copolymer's transition temperature, as shown in Figure 5. For all four studied compositions, $T_g$ increased with the content of CB increasing, albeit to a small extent. The influence of CB on $T_g$ indicated some kind of interaction between the CB particles and the polymer. When the polymer segments were bound to the rigid CB particles, the molecular motion was restricted in the vicinity of the particles, so $T_g$ rose. When the BA monomer content was greater in the copolymer (which resulted in greater interaction with CB), the phenomenon of $T_g$ rising with the content of CB increasing was more significant.
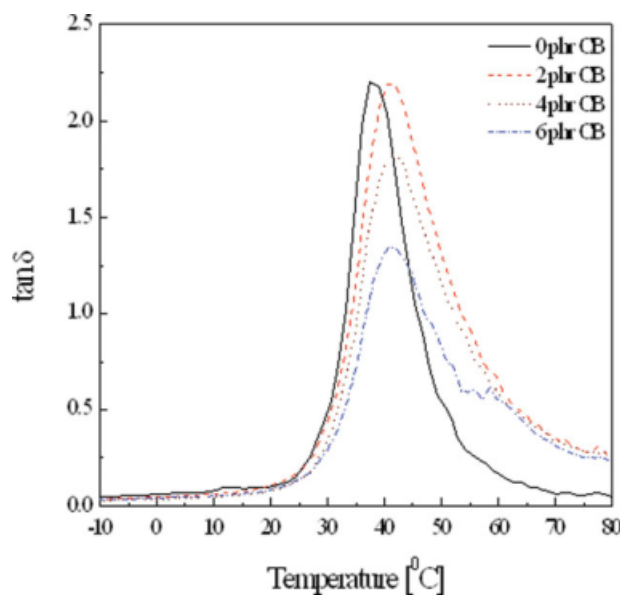
**Figure 6** Effect of the addition of CB on tan δ of the St–BA copolymer containing 50% BA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
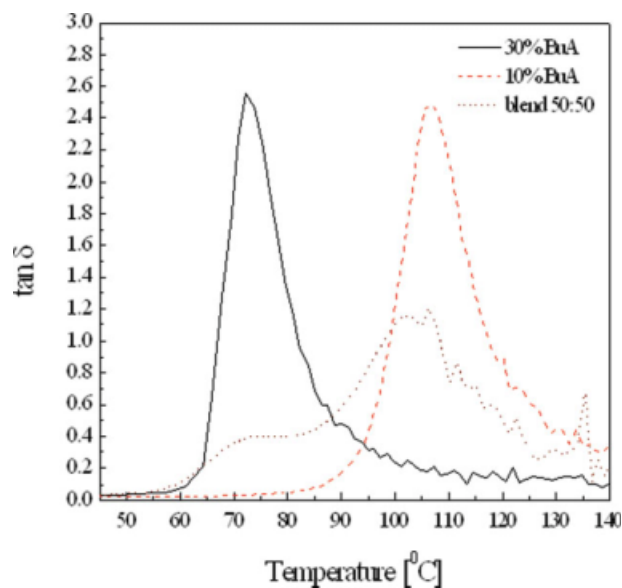
**Figure 7** Effect of blending two different St–BA copolymer latices on tan δ. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 demonstrates the effect of CB on the dynamic mechanical properties. Interestingly, the damping levels of the St–BA copolymers were extremely high (beyond tan δ = 2.2). The damping temperature range was approximately 25–40°C. The addition of CB reduced the damping peak, but still, even with the highest content of CB studied, the damping levels were beyond tan δ = 1, which may be sufficient for practical damping. The damping temperature range hardly changed with increasing CB content. Interestingly, upon the addition of CB, damping increased at temperatures beyond $T_g$. Hence, the copolymer became a better vibration-damping material, damping within a wider temperature range. The reason for the high damping level above $T_g$ could be CB particle–particle friction. As expected, the damping decreased with increasing CB content.

The influence of DBSA on the St–BA copolymer was examined with a 50% BA copolymer with 6 phr CB with different concentrations of DBSA. It was found (not shown) that the influence of DBSA on the dynamic mechanical properties of the St–BA copolymer was insignificant.

A blend of two copolymers of different compositions was investigated. A copolymer with 30% BA was blended with a copolymer containing 10% BA. Equal amounts of the two copolymer emulsions were mechanically mixed without any additives. The tan δ peak of the blended sample (see Fig. 7) is composed of two peaks and, therefore, is wider and spread over the temperature range of the two peaks

of its constituents. From a technical damping point of view, the wide tan δ peak is advantageous. It means a wide range of temperatures in which the polymer is capable of vibration damping. Even though the tan δ peak is lower than the two original peaks, the peak height is still above 0.3 for a wide temperature range of approximately 60°C, in contrast to approximately 25–40°C for the single copolymer samples. Thus, the damping temperature range can be varied through changes in the compositions of the blended emulsion polymers.

## CONCLUSIONS

Blending CB with St–BA polymer emulsions significantly reduced the percolation threshold. The incorporation of CB within the emulsions was carried out with the help of a dispersant (DBSA). DBSA further decreased the percolation threshold because of the better CB dispersion that it provided. On the other hand, the small amount of added DBSA did not influence the dynamic mechanical properties of the St–BA random copolymer. The composition of the random copolymer had a strong effect both on the electrical conductivity and on $T_g$. As the content of BA in the copolymer increased, the percolation threshold increased. The damping levels of the St–BA copolymers were extremely high, whereas the damping range was quite wide (25–40°C). Through the blending of two St–BA copolymers of different compositions, the damping range could become much wider. The addition of CB reduced the damping, but the tan δ peaks were still significantly high even at the highest CB content studied.

## References

1. Aklonis, J. J.; Macknight, W. J. Introduction to Polymer Viscoelasticity, 2nd ed.; Wiley-Interscience: New York, 1983.
2. Hu, R.; Dimonie, V. L.; El-Aasser, M. S.; Pearson, R. A.; Hiltner, A.; Milonakis, S. G.; Sperling, L. H. J Polym Sci Part B: Polym Phys 1997, 35, 1501.
3. Ferry, J. D. Viscoelastic Properties of Polymers, 2nd ed.; Wiley: New York, 1970.
4. Mark, H. Encyclopedia of Polymer Science and Engineering; Wiley: New York, 1985; Vol. 5, p 299.
5. Oksman, K.; Lindman, H. J Appl Polym Sci 1998, 68, 1845.
6. Nielsen, L. E. Mechanical Properties of Polymers and Composites; Marcel Dekker: New York, 1974.
7. Kwak, G. H.; Inoue, K.; Tominaga, Y.; Asai, S.; Sumita, M. J Appl Polym Sci 2001, 82, 3058.
8. Corasaro, R. D.; Sperling, L. H. Sound and Vibration Damping with Polymers; ACS Symposium Series 424; American Chemical Society: Washington, DC, 1989.
9. Ghosh, S.; Khastgir, A. D.; Bhowmick, A. K. J Appl Polym Sci 1998, 67, 2015.
10. Donnet, J. B. Carbon Black: Science and Technology, 2nd ed.; Marcel Dekker: New York, 1993.

11. Carmona, F. Presented at the 2nd International Conference on Carbon Black, Moulhouse France, Sept 27, 1993.
12. Leyva, M. E.; Barra, G. M. O.; Moriera, A. C. F.; Soares, B. G.; Khastgir, D. J Polym Sci Part B: Polym Phys 2003, 41, 2983.
13. Feng, J.; Chan, C. M. Polym Eng Sci 1998, 38, 1649.
14. Tchoudakov, R.; Breuer, O.; Narkis, M.; Siegmann, A. Polym Eng Sci 1996, 36, 1336.
15. Gubbels, F.; Blacher, S.; Vanlathem, E.; Jerome, R.; Deltour, R.; Brouers, F.; Teyssie, P. Macromolecules 1995, 28, 1559.
16. Grunlan, J. C.; Gerberich, W. W.; Francis, L. F. J Appl Polym Sci 2001, 80, 692.
17. Grunlan, J. C.; Gerberich, W. W.; Francis, L. F. Polym Eng Sci 2001, 41, 1947.
18. Grunlan, J. C.; Ma, Y.; Grunlan, M. A.; Gerberich, W. W.; Francis, L. F. Polymer 2001, 42, 6913.
19. Grunlan, J. C.; Mehrabi, A. R.; Bannon, M. V.; Bahr, J. L. Adv Mater 2004, 16, 150.
20. Grunlan, J. C.; Bloom, F. L.; Gerberich, W. W.; Francis, L. F. J Mater Sci Lett 2001, 20, 1523.