

DMA Analysis of the Damping of Ethylene–Vinyl Acetate/Acrylonitrile Butadiene Rubber Blends

X. Y. Shi, W. N. Bi, S. G. Zhao

School of Polymer Science and Engineering, Key Laboratory of Rubber-plastics, Ministry of Education, Qingdao University of Science and Technology, Qingdao 266042, China

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ABSTRACT: The mechanical and damping properties of blends of ethylene–vinyl acetate rubber (VA content > 40% wt) (EVM)/acrylonitrile butadiene rubber (NBR), with 1.4 phr BIPB [bis (*tert*-butyl peroxy isopropyl) benzene] as curing agent, were investigated by DMA and DSC. The effect of chlorinated polyvinyl chloride (CPVC), silica, carbon black, and phenolic resin (PF) as a substitute curing agent, on the damping and mechanical properties of EVM/NBR blends were studied. The results showed that 10 phr CPVC did not contribute to the damping of EVM700/NBR blends; Silica could dramatically improve the damping of EVM700/NBR blends because of the formation of bound rubber between EVM700/NBR and silica, which appeared as a shoulder $\tan \delta$ peak between 20 and 70°C proved by DMA and DSC. This shoulder $\tan \delta$ peak increased as the increase of the content of EVM in

EVM/NBR blends. The tensile strength, modulus at 100% and tear strength of the blend with SiO₂ increased while the elongation at break and hardness decreased comparing with the blend with CB. PF, partly replacing BIPB as the curing agent, could significantly improve the damping of EVM700/NBR to have an effective damping temperature range of over 100°C and reasonable mechanical properties. Among EVM600, EVM700, and EVM800/NBR/silica blend system, EVM800/NBR/silica blend had the best damping properties. The EVM700/NBR = 80/10 blend had a better damping property than EVM700/NBR = 70/20. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2234–2239, 2012

Key words: ethylene–vinyl acetate rubber; damping; nitrile butadiene rubber; silica

INTRODUCTION

Polymers have been widely applied in space navigation, transportation, mechanical equipment, construction, and daily life for achieving acoustic and vibration damping due to a unique combination of low modulus and inherent damping. The height and width of the $\tan \delta$ peak at glass transition zone are the two main factors to estimate the damping of a material^{1–3}. However, homopolymers usually exhibit effective damping ($\tan \delta > 0.3$) in a narrow temperature range of 20–30°C around their glass transition temperatures (T_g), during which the polymers have pronounced dissipation of the mechanical energy as heat based on the onset of coordinated chain molecular motion^{4,5}. Thus blending two or more rubbers has been used as an effective way to obtain damping materials with an enlarged temperature range^{6,7}.

Ethylene–vinyl acetate (EVM) is the accepted abbreviation for EVM copolymers with between 40 and 90% vinyl acetate (VA) and having elastomeric properties. The peak value of the damping factor $\tan \delta$ of EVM (Levapren 600, Levapren 700, and Levap-

ren 800; VA = 60, 70, and 80 wt %, respectively; manufactured by Lanxess Deutschland GmbH, Germany) was higher than 0.90 because of abundant ester side groups and its glass transition temperature zone was between –20 and 40°C, which happens to be the use temperature of many damping materials. So EVM could be a good choice as a damping material^{8,9}.

Acrylonitrile butadiene rubber (NBR) have been used as damping materials due to their high $\tan \delta$ values^{10–14}, so blending with EVM could enlarge the damping peak zone and produce a multifunctional damping material with good oil and ozone resistance, thermostability, and flame-retardance.

In this research, a Haake torque rheometer was employed to blend EVM with NBR. The effects of PVC, CPVC, silica, carbon black, and PR on the mechanical and damping properties were examined to provide some reference data for preparation of high damping materials with wider effective damping temperature range.

EXPERIMENTAL

Materials

Nitrile-butadiene rubber (NBR-Perbunan3470; AN = 34 wt %; Table I) and ethylene vinyl acetate copolymer rubber (Levapren 600, Levapren 700, and

Correspondence to: X. Y. Shi (lindashi88@hotmail.com).

TABLE I
Recipes

Materials	1#	2#	3#	4#	5#	6#	7#	8#	9#	10#	11#
EVM700	70	70		80	45	45			45		
NBR3470	20	20	20	10			20	10		20	10
EVM800			70		45		70	80			
EVM600						45				70	80
CPVC	10	10	10	10	10	10	10	10	10	10	10
SiO ₂	30		30	30	30	30	30	30	30	30	30
DCP	1.4	1.4	0.8	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
N330		30									
Phenolic Resin				3							
SnCl ₂				1							

Levapren 800; designated EVM600, EVM700, and EVM800 with VA contents of 60, 70, and 80 wt %, respectively) were obtained from Lanxess Deutschland GmbH (Germany). PVC (S-1000) was obtained from Qilu Branch of SINOPEC (China), CPVC (67.3 wt % Cl) from Qingdao Sanyou Chemical Company (China), phenolic resin (PF) (SP1045) from Schenectady International (Shanghai, China), precipitated silica from Shandong Haihua Silica Factory (China), BIPB [bis (*tert*-butyl peroxy isopropyl) benzene] from Rhein Chemie (Qingdao) and carbon black (N330) from Evonik Qingdao Industries AG (China). SnCl₂ was bought from the local market.

Sample preparation

EVM and NBR were first mixed in a Haake Rheomix 30000S mixer for about 2–3 min at 80°C (if blended with CPVC, at 140°C) at a rotor speed of 50 rpm.

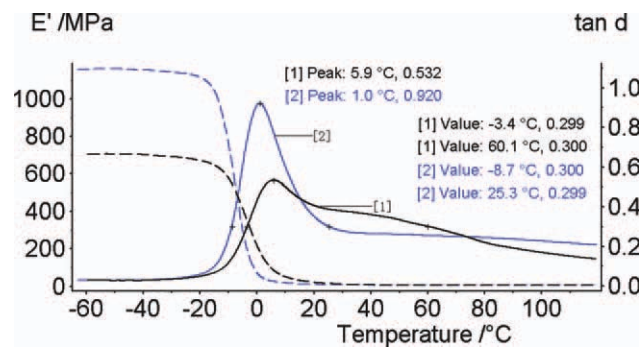


Figure 1 DMA curves of EVM700/NBR blends. (a) EVM700/NBR/SiO₂ = 70/20/30; (b) EVM700/NBR/CB = 70/20/30. Note: The “value” in the figure refers to the temperature corresponding to tan δ = 0.3; the right value—the left value = EDTR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Then silica was added and mixed for about 7–8 min. Lastly, BIPB was put in and mixed until the torque became constant. All blends below were cured with BIPB unless stated. The blends were taken out of the mixer and processed on an SK-160B two-roll mill (if compounding with PVC or CPVC, at 80°C) manufactured by Shanghai Plastics and Rubber Machinery Factory, China, and then molded into sheets in a VC-150T-FTMO-3RT vacuum press manufactured by Jiabin Electric Company, China, at 180°C for 8 min.

Measurements

Tensile testing was carried out using an AI-7000S Universal Material Tester, manufactured by Taiwan

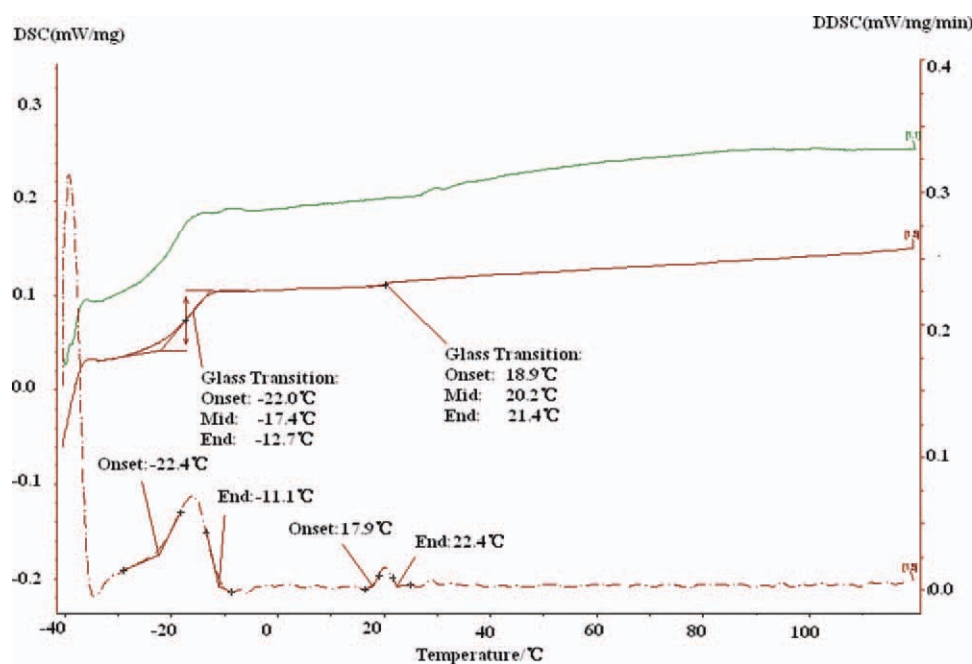


Figure 2 DSC curve of EVM700/NBR/SiO₂ = 70/20/30. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

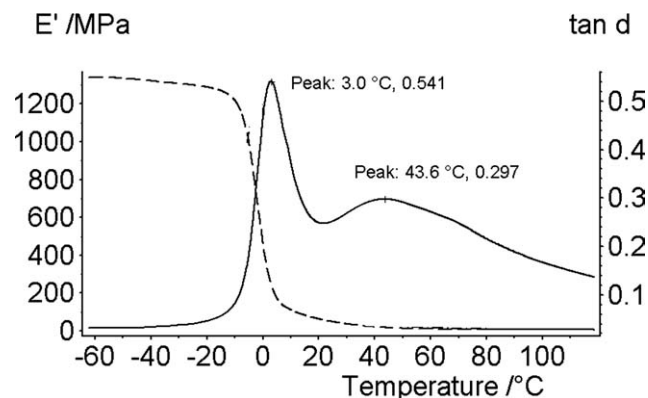


Figure 3 DMA curve of EVM700/NBR/SiO₂ = 80/20/30.

Gaotie Company, at a tensile speed of 500 mm/min according to ISO 37 : 1994.

The dynamic mechanical analysis was carried out on a Netzsch DMA 242 Dynamic Mechanical Analyzer, manufactured by Netzsch Company, Germany, from -60 to 120°C at a heating rate of 3 K/min and a fixed frequency of 10 Hz in a mode of double cantilever deformation. Curves of $\tan \delta$ and E' as a function of temperature were examined.

The DSC curves were produced using a Netzsch DSC 204 F1, manufactured by Netzsch Company, Germany, from -40 to 120°C at a heating rate of 10 K/min .

RESULTS AND DISCUSSION

Effect of fillers on the mechanical and damping properties of EVM700/NBR

Silica and CB were chosen as the filler in the blends. The effect of fillers on the damping of EVM700/NBR blends is shown in Figure 1.

CPVC has polar side atoms and a T_g of 89°C ¹⁵. Introducing CPVC to the blends might be expected to expand the effective damping temperature range (abbreviated as EDTR) in the higher temperature area. So all the EVM/NBR blends below were mixed with 10 phr CPVC unless stated.

It can be seen in Figure 1 the peak value of $\tan \delta$ of EVM700/NBR/SiO₂ was 0.532 with corresponding T_g of 5.9°C and an effective damping temperature range (EDTR) ($\tan \delta > 0.3$) of 63.5°C . The peak value of $\tan \delta$ of EVM700/NBR/CB was 0.920 with corresponding T_g of 1.0°C and an EDTR of 34.0°C . It

indicated that in EVM700/NBR blends added 30 phr silica significantly reduced the damping peak to 0.532 from 0.920 of CB filled blend, but increased the $\tan \delta$ value between 20 and 70°C . This was attributed to the glass transition of the restricted EVM/NBR layer surrounding the silica particles^{16–18}. It was also deduced that the new damping peak was not derived from CPVC since 10 phr CPVC was mixed in the both blends.

To further prove the second T_g at 20 – 70°C , a DSC test for EVM700/NBR/SiO₂ = 70/20/30 (Curve¹ in Fig. 1) is shown in Figure 2. It can be seen that there are two glass transition temperatures $T_{g1} = -17.4^{\circ}\text{C}$ and $T_{g2} = 20.2^{\circ}\text{C}$ corresponding to the obvious damping peak at 5.9°C and the weak peak at 20 – 70°C in DMA curve. To prove the weak peak is not from CPVC, a DMA test for EVM700/NBR/SiO₂ = 80/20/30 without CPVC at a lower frequency of 1 Hz was carried out and shown in Figure 3. The weak peak became more obvious with T_g of 43.6°C and $\tan \delta$ peak value of 0.297, which was neither from EVM nor from NBR. This indicated that a new chain relaxation occurred in EVM700/NBR blend at the presence of silica instead of CB. This was attributed to the stronger interaction between EVM/NBR and silica because of the generation of hydrogen bonds attributed to the abundant $-\text{OH}$ groups on the surfaces of silica particles and the $\text{C}=\text{O}$ group in EVM¹⁹ and the $-\text{CN}$ group in NBR²⁰.

The effect of silica and CB on the mechanical properties of EVM700/NBR blends is shown in Table II. The tensile strength, modulus at 100% and tear strength of the blend with SiO₂ increased while the elongation at break and hardness decreased comparing with the blend with CB. This indicated that silica had better reinforcement for EVM700/NBR blends than carbon black because of the creation of hydrogen bonds between silica and EVM and NBR.

Effect of curing agent on the mechanical and damping properties of EVM800/NBR

PF, a possible crosslinking agent for rubber containing double bonds, was used as a substitute of BIPB to cure NBR in the blends. The effect of PF on the damping of EVM800/NBR is shown in Figure 4. The peak value of $\tan \delta$ of EVM800/NBR/BIPB = 70/20/1.4 was 0.869 with corresponding T_g of 18°C and

TABLE II
Effect of Fillers on the Mechanical Properties of EVM/NBR Blends

Recipe	Tensile strength (MPa)	Modulus at 100% (MPa)	Elongation at break (%)	Hardness/shoreA	Tear strength (N/mm)
EVM700/NBR/SiO ₂ = 70/20/30	12.8	8.6	144	77	32.0
EVM700/NBR/CB = 70/20/30	10.5	6.5	164	87	27.7

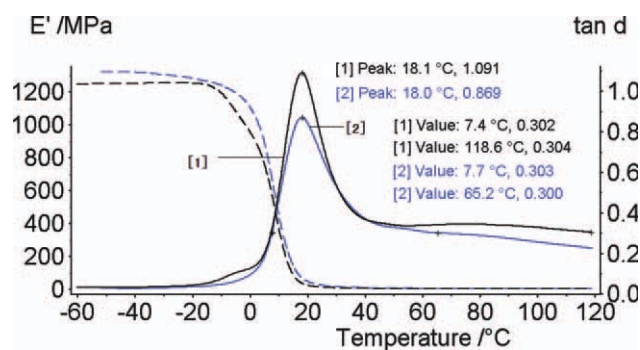


Figure 4 DMA curves of EVM800/NBR blends (30 phr SiO₂ mixed in the blends). (a) EVM800/NBR/BIPB/PR/SnCl₂ = 70/20/0.8/3/1. (b) EVM800/NBR/BIPB = 70/20/1.4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

an EDTR of 57.4°C. There was not an obvious weak peak like EVM700/NBR blend at about 40°C in Figure 3. This might be because the weak peak was too close to the original T_g to be seen. The peak value of

$\tan \delta$ of EVM800/NBR/BIPB/PR/SnCl₂ = 70/20/0.8/3/1 increased to 1.091 and the EDTR was expanded to 111.2°C, which appeared the blend had a good damping property from 7.4 to 118.6°C. It is presumed that PR and BIPB cured different components in different phases and respectively, generated shorter crosslinking network, which consequently caused more chains movements and more inner friction. It also can be deduced that PR disturbed BIPB effectively curing EVM phase, which caused lower crosslink density in the matrix EVM phase. By comparing the mechanical properties of the two blends shown in Table III, it can be seen that the blend cured by PR had lower strength and modulus at 100% and higher elongation at break, which indicated a lower crosslinking density. However, higher hardness and tear strength indicated the interact-locked different crosslinking networks.

The DSC curves for the above two blends are shown in Figures 5 and 6. Figures 5 and 6 both only showed one T_g . This is in according with DMA curves in Figure 4.

TABLE III
Effect of Different Curing Agents on Mechanical Properties of EVM/NBR Blends

Recipe	Tensile strength (MPa)	Modulus at 100% (MPa)	Elongation at break (%)	Hardness/shoreA	Tear strength (N/mm)
EVM800/NBR/BIPB/PR/SnCl ₂ = 70/20/0.8/3/1	9.6	4.5	297	80	39.9
EVM800/NBR/BIPB = 70/20/1.4	11.2	7.2	160	78	35.0

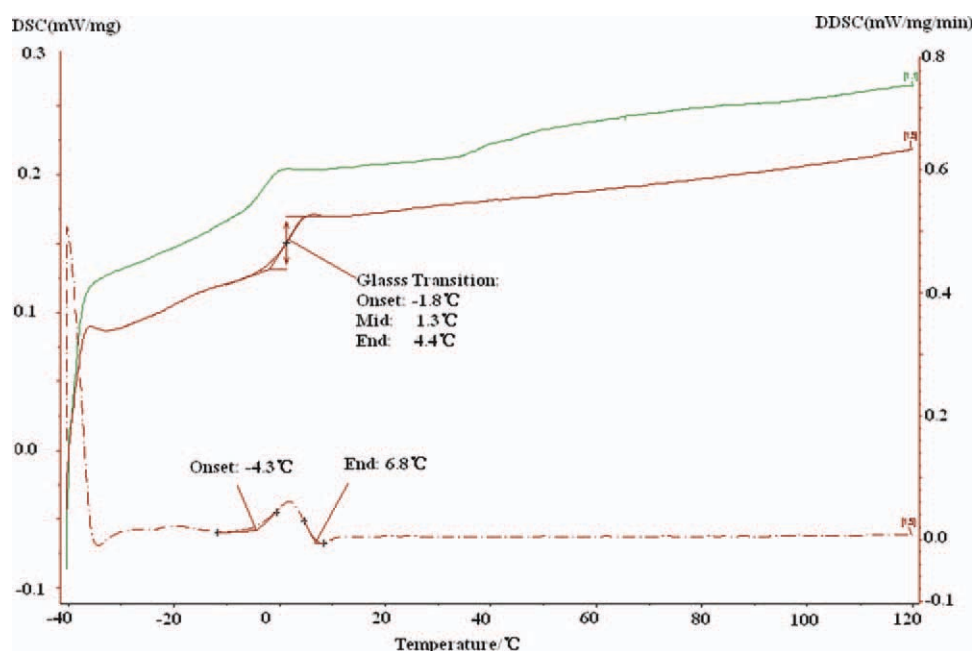


Figure 5 DSC curve of EVM800/NBR/BIPB/PR/SnCl₂ = 70/20/0.8/3/1 (30 phr SiO₂ mixed in the blend). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

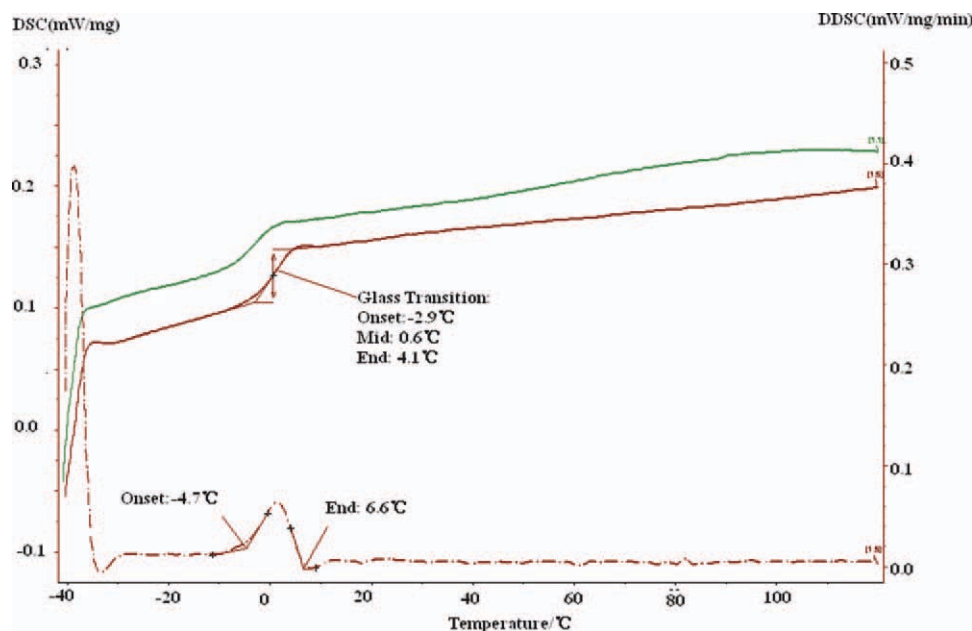


Figure 6 DSC curve of EVM800/NBR/BIPB = 70/20/1.4 (30 phr SiO₂ mixed in the blend). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of EVM with different VA content on the mechanical and damping properties of EVM/NBR

The DMA curves of blends of EVM700/NBR = 80/10 and EVM600/NBR = 80/10 (both cured by BIPB and mixed with 30 phr silica) are shown in Figure 7. The peak value of $\tan \delta$ of EVM700/NBR = 80/10 was 0.752 with corresponding T_g of 1.6°C and an EDTR of 71.8°C, which was 8.3°C wider than that of EVM700/NBR = 70/20 in Figure 1 and mostly attributed to the weak peak between 40 and 60°C. The peak value of $\tan \delta$ of EVM600/NBR = 80/10 was 0.641 with corresponding T_g of -6.7°C and a much lower EDTR of 24.3°C. A weak peak could also be seen in EVM600/NBR = 80/10 between 30 and 60°C in Figure 7. However, the value of the weak peak was lower than 0.3 and did not contribute to the EDTR. This indicated that EVM600 like

EVM700 could create bound rubber with silica and emerge as a weak peak in DMA curve. Furthermore, the weak peak increased as the increase of the content of EVM in EVM/NBR/silica system.

The DMA curves of blends of EVM700/NBR = 80/10 and EVM800/NBR = 80/10 (both cured by BIPB and mixed with 30 phr silica) are shown in Figure 8. Comparing with EVM700/NBR = 80/10, the peak value of $\tan \delta$ of EVM800/NBR = 80/10 increased to 0.834 from 0.752 and the corresponding T_g moved to 18.4°C from 1.6°C and the EDTR was expanded to 79.7 from 71.8°C. The weak peak could also be seen in EVM800/NBR = 80/10 between 40 and 60°C in Figure 8, which was much obvious than that in EVM800/NBR = 70/20 in Figure 4. This further proved that the weak peak increased as the increase of the content of EVM in EVM/NBR/silica

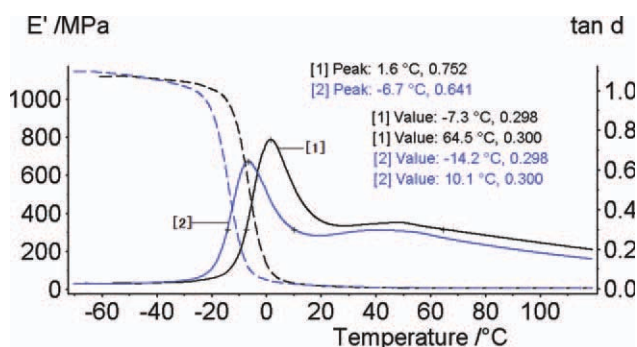


Figure 7 DMA curves of EVM700/NBR = 80/10 and EVM600/NBR = 80/10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

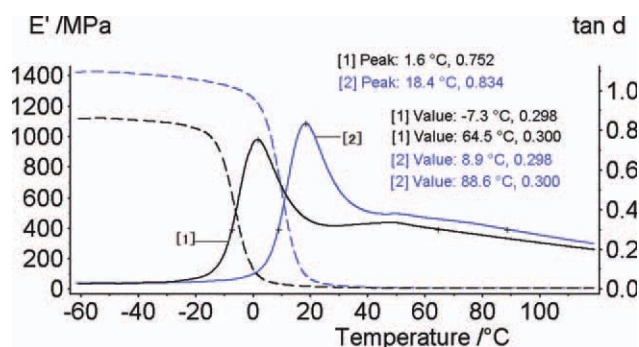


Figure 8 DMA curves of EVM700/NBR = 80/10 and EVM800/NBR = 80/10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

system. That is the bound rubber generated in EVM/NBR/silica blend increased as the increase of the content of EVM.

CONCLUSIONS

CPVC (10 phr) did not show as an obvious $\tan \delta$ peak in the DMA curve of EVM700/NBR blend and consequently did not contribute to the damping of EVM700/NBR blends.

Silica could dramatically improve the damping of EVM700/NBR blends because of the formation of bound rubber between EVM700/NBR and silica, which appeared as a weak $\tan \delta$ peak between 20 and 70°C proved by DMA and DSC. The weak peak increased as the increase of the content of EVM in EVM/NBR blends. The tensile strength, modulus at 100%, and tear strength of the blend with SiO₂ increased while the elongation at break and hardness decreased comparing with the blend with CB.

PF, partly replacing BIPB as the curing agent, could significantly improve the damping of EVM700/NBR to have an effective damping temperature range of over 100°C and reasonable mechanical properties.

Among EVM600, EVM700, and EVM800/NBR/silica blend systems, EVM800/NBR/silica blend had the best damping properties. The EVM700/NBR = 80/10 blend had a better damping properties than EVM700/NBR = 70/20.

References

1. Mok, M.; Kim, J.; Torkelson, J. M. *J Polym Sci Part B: Polym Phys* 2008, 46, 48.
2. Wu, J. H.; Li, C. H.; Chiu, H. T.; Shong, Z. J.; Tsai, P. A. *J Thermoplastic Compos Mater* 2009, 22, 503.
3. Kaneko, H.; Inoue, K.; Tominaga, Y.; Asai, S.; Sumita, M. *Mater Lett* 2002, 52, 96.
4. Ratna, D.; Manoj, N. R.; Chandrasekhar, L. *Polym Adv Technol* 2004, 15, 583.
5. Fahrenholtz, S. R.; Kwei, T. K. *Macromolecules* 1981, 14, 1076.
6. Wu, C.; Wei, C.; Guo, W.; Wu, C. *J Appl Polym Sci* 2008, 109, 2065.
7. Qin, C. L.; Cai, J. *Comp Chem Phys* 2004, 85, 402.
8. Shi, X. Y.; Liang, Y. C.; Zhang, P. *Synth Rubber Ind* 2006, 29, 458.
9. Shi, X. Y.; Zhang, P.; Liang, Y. C.; Ren, C. L. *J Macromol Sci Part B: Polym Phys* 2007, 46, 807.
10. Varghese, H.; Johnson, T.; Bhagawan, S. S.; Joseph, S.; Thomas, S.; Groeninckx, G. *J Polym Sci Part B: Polym Phys* 2002, 40, 1556.
11. Xiang, P.; Zhao, X. Y.; Xiao, D. L.; Lu, Y. L.; Zhang, L. Q. *J Appl Polym Sci* 2008, 109, 106.
12. Patri, M.; Samui, A. B.; Deb, P. C. *J Appl Polym Sci* 1993, 48, 1709.
13. Manoj, N. R.; De, P. P. *Polymer* 1998, 39, 733.
14. Senake Perera, M. C.; Ishiaku, U. S.; Mohd Ishak, Z. A. *Eur Polym J* 2001, 37, 167.
15. Zhang, L. C. *Chem Ind Press* 2000, 109.
16. Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* 1995, 28, 396.
17. Chen, L.; Zheng, K.; Tian, X.; Hu, K.; Wang, R.; Liu, C.; Li, Y.; Cui, P. *Macromolecules* 2010, 43, 1076.
18. Shi, X. Y.; Bi, W. N. *J Macromol Sci Phys* 2011, 50, 417.
19. Shi, X. Y.; Zhao, F.; Zhai, J. X.; Zhao, S. G. *J Macromol Sci Phys* 2008, 47, 1211.
20. Choi, S. S. *Polym Test* 2002, 21, 201.