Developments of High Performance Vibration Absorber from Poly(vinyl chloride)/Chlorinated Polyethylene/Epoxidized Natural Rubber Blend

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ABSTRACT: A high performance vibration absorber requires a high loss factor behavior over a wide temperature and frequency range. An investigation was carried out to prepare such materials based on poly(vinyl chloride), chlorinated polyethylene, and epoxidized natural rubber ternary blends. The loss factor and damping behavior of several compositions were measured using a viscoelastic spectrometer and a polymer-laminated steel cantilever-beam damping device. Suitable compositions were found to give good mechanical properties and high loss factor over a wide temperature and frequency range. It was also observed that flake-type fillers improve the damping behavior. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 855–863, 1999

Key words: vibration; absorber; poly(vinyl chloride); chlorinated polyethylene; epoxidized natural rubber

INTRODUCTION

Polymeric viscoelastic materials are of general use for vibration absorbers. For this function, the magnitude of the loss tangent is very important. The maximum loss factor of a polymeric material is obtained at the glass transition temperature (T_g). The antivibration behavior of vibration absorbers, however, depends on the loss factor at the application and ambient temperatures. A number of authors have reported on high performance vibration absorbers having a high loss factor over a wide temperature range. The materials investigated so far include blends of polymers having different T_g such as poly(vinyl chloride) (PVC)/ethylene vinyl acetate,[1] a few blends of acrylic ester polymers,[2] and some types of styrene–butadiene copolymer.[3] As far as the blends are concerned, if moderate miscibility of the binary or ternary blends is achieved, a wider temperature range for a high loss factor could be obtained. This is the most important factor for excellent vibration absorbers. In other words, neither miscible nor immiscible blends are of use for vibration absorbers.

Several studies on PVC/epoxidized natural rubber (ENR) blends have been reported in terms of optimum blending conditions,[4] mechanical and morphological properties,[5] rheological properties, and miscibility behavior.[6–9] Unplasticized and

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Table I Details of Materials and Fillers

Materials	Abbrev./Code	Description	Source
Poly(vinyl chloride)	PVC	103EP (P = 1050)	Nippon Zeon
Chlorinated polyethylene	CPE		Daiso
	G-235	35% Cl (5% cryst.)	
	H-135	35% Cl (amorp.)	
	G-220	22% Cl (5% cryst.)	
	G-245	45% Cl (amorp.)	
Epoxidized natural rubber	ENR25	25 mol % epoxidation	Kumpulan
	ENR50	50 mol % epoxidation	Guthrie
Dibutyl-tin-dimaleate	MA300A	Stabilizer for PVC	Nitto Kasei
Dioctyl-tin-dilaurate	#8501		
Dioctyl-tin-dimaleate	#8813		
			Kyodo
Dibutyl-tin-mercapto-propyonate	KS-42B-6		Yakuhin
Polyethylene wax	AC-6A	Lubricant	Allied Signal
Fillers and Product Names	**Average Size**	**Shape**	**Source**
Calcined clay, Burgess #30	1.5 μm	Flake	Burgess Pigment
Crown clay	<2 μm	Granular	Southeastern clay
Silica, Nipsil VN-3	160 nm	Granular	Nippon Silica
Carbon black, Seast SO	45 nm	Granular	Tokai Carbon
Phlogopite mica, Suzorite 325S	40 μm	Flake	Kurare
Muscovite mica DG4K	50 μm	Flake	Shiraishi Calcium
Graphite CP-2	11 μm	Flake	Fuji Kokuen
Wollastonite			
NYAD 325	<35 μm	Needle	NYCO
NYAD 400	<44 μm	Needle	

plasticized PVCs were found miscible with ENR (50 mol % epoxidation), showing a single T_g.[7–9] For PVC/chlorinated polyethylene (CPE) blends, the chlorine content and the distribution of chlorine content (DCC) of CPE seems to be an important factor in the miscibility behavior. PVC/CPE blends were found to be immiscible when CPE (chlorinated in water) with less than 45 wt % chlorine was used.[10] However, with CPE (chlorinated in an organic solvent) containing 48 wt % chlorine, the blends were miscible at some blend ratios.[11] This difference is due to the chlorine content and DCC. CPE that is chlorinated by the solution method has a relatively uniform DCC.[12] The role of ENR as a compatibilizer for the PVC/CPE system was also investigated.[13] It was concluded that for blends containing chlorinated polyhydrocarbon with 48% chlorine content or higher, ENR may be used as an effective compatibilizer.

In this study, the potential of a PVC, CPE, and ENR ternary blend as a vibration absorber temperature and frequency range is reported. Various shape fillers were added to this ternary system to investigate their effect on the damping behavior. Flake shape fillers (e.g., graphite) have been observed to improve the damping properties.[14]

The first part of this report focuses on the miscibility behavior of CPE/ENR and PVC/ENR binary blends and identifies the effect of ENR (amount and mole percent epoxidation) and CPE (with 45 wt % chlorine content or less) on the associated properties of PVC/CPE/ENR ternary blends. Subsequently, a suitable composition of the ternary blend was identified; using various fillers the materials were evaluated for their mechanical properties, dynamic mechanical properties, and damping behavior.

EXPERIMENTAL

The materials used in this experiment are detailed in Table I. The mixing was carried out as follows:

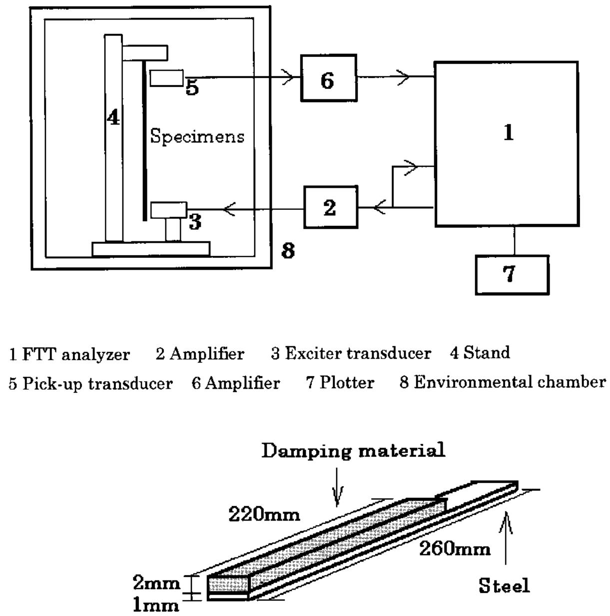

Figure 1 Cantilever-beam test device and test specimens.

1. Unfilled polyblend: ENR and the lubricant were mixed with an 8-in. two-roll mill at room temperature for 15 min. PVC, CPE, stabilizers, and lubricant had been premixed in a beaker and were incorporated into the ENR with an 8-in. two-roll mill at 170°C for 5 min. The mixtures were compression molded at 150°C for 5 min to prepare the sheets for subsequent testing.
2. Filled polyblend: Filler and other ingredients were mixed with the prepared unfilled polyblends using a kneader mixer at 130°C for 5 min. The resultant mixtures were roll milled at 130°C for 1 min. Compression molding was carried out as described previously.

The tensile test of the molded materials was performed according to JIS procedure K-6301 at 23°C with crosshead speed of 20 cm/min. The hardness was expressed in JIS A and Shore D. The tan δ was determined with a viscoelastic spectrometer (Iwamoto Seisakusho Ltd., VES-F3) at a frequency of 10 Hz and a heating rate of 2°C/min. A $2 \times 4 \times 35$ mm specimen dimension was used. The measurement of the damping factor η was performed according to JIS procedure G-0602 using cantilever-beam type laminated steel. The block diagram of the experimental setup is shown in Figure 1. The material to be tested was laminated to the steel with an epoxy resin adhesive.

RESULTS AND DISCUSSION

Binary Blends

The recipes of the binary blends investigated and their respective tensile and hardness properties are shown in Table II. It is apparent that recipes 1 and 2 are poor blends in terms of mechanical

Table II Recipes and Properties of Binary Blends

	1	2	3	4	5
Recipes (phr)					
CPE					
G-235	50			50	
H-135		50			50
ENR50	50	50	50		
PVC			50	50	50
MA300A			1	1	1
#8501			0.5	0.5	0.5
WB-16	1	1	1		
Tensile and hardness properties					
M100 (MPa)	0.6	0.8	11.1	10.1	10.1
TS (MPa)	3.2	1.7	17.7	10.6	14.2
EB (%)	730	355	435	140	220
Hardness					
JIS A	54	45	94	95	93
Shore D	12	10	53	50	47

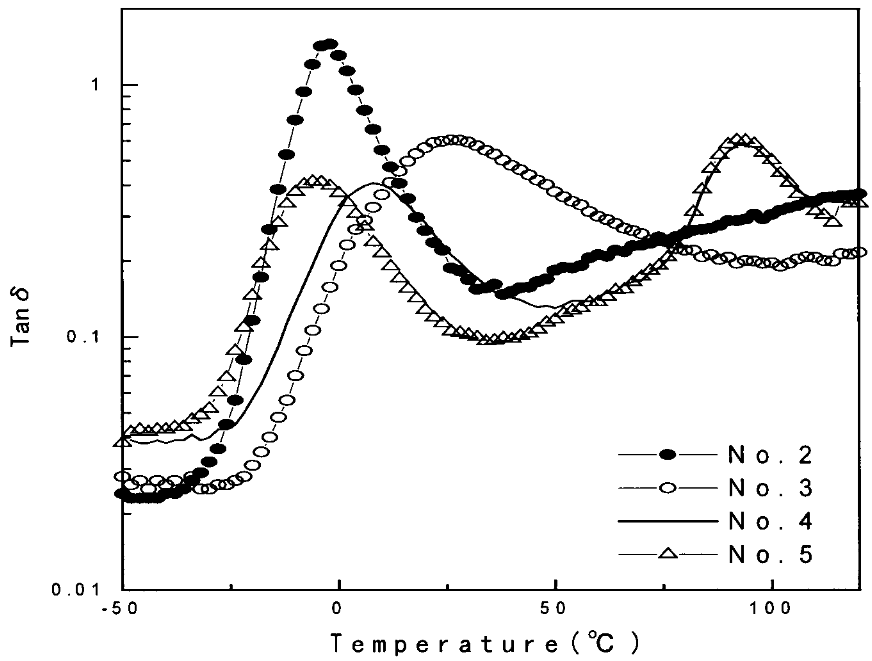

Figure 2 Tan delta of the binary blends as a function temperature.

properties. The temperature dependence of the tan δ of the blends is shown in Figure 2. The single tan δ peak of the CPE/ENR (2) indicates that the blend is miscible. This is consistent with a previous study in which ENR was found miscible with chlorinated polymers due to specific interactions between the oxirane group and the chlorine atom.[15] On the other hand, the PVC/CPE blends (4 and 5) gave split peaks of typical immiscible blends. This was expected because the chlorine content of the CPEs was less than 48 wt %. Between these two blends, however, there was a significant difference in terms of the degree of splitting of the two peaks, in spite of the same chlorine content. This difference was probably due to the DCC factor. G-235 (5% crystallinity) has a broader DCC and higher T_g than H-135 (amorphous).[12,16] This showed that the higher chlorinated part of G-235 was tweaked by the chlorine atoms of the PVC.

Unfilled Ternary Blends

The compositions and mechanical properties of the ternary blends with different type of CPEs are given in Table III in which the blend ratio is kept at 1 : 1 : 1. Recipe 7, which used CPE with 5% crystallinity, gave significantly lower tensile properties. The tan δ behavior of the blends from 0 to 100°C shown in Figure 3 suggests that the amorphous CPEs (H-135 and G-245) are preferred. This is because the degree of splitting and intensity of the tan δ peaks for these two CPEs are less pronounced, indicating better miscibility. The data suggest that ternary blends with rea-

Table III Recipes and Properties of PVC/ENR 50/CPE Ternary Blends

	6	7	8	9
Recipes (phr)[a]				
PVC	33.3	33.3	33.3	33.3
ENR 50	33.3	33.3	33.3	33.3
CPE				
G-220	33.3			
G-235		33.3		
H-135			33.3	
G-245				33.3
Tensile and hardness properties				
M100 (MPa)	8.1	6.4	7.9	8.1
TS (MPa)	15.4	9.0	15.8	11.8
EB (%)	500	360	530	500
Hardness				
JIS A	93	93	94	93
Shore D	45	42	50	45

[a] Plus MA300A (1 phr), #8501 (0.5 phr), and WB-16 (1 phr).

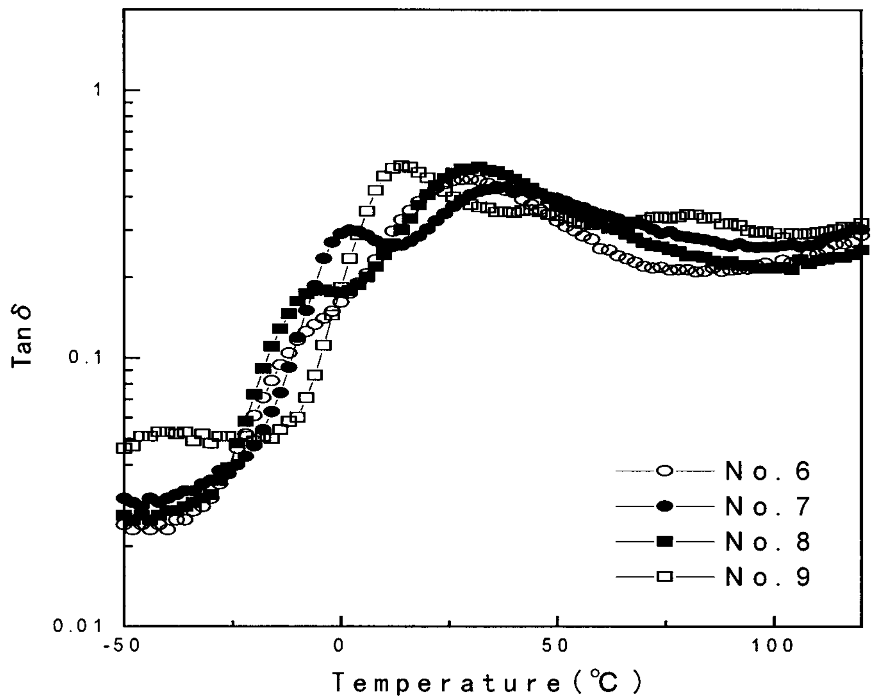

Figure 3 The temperature dependence of tan delta behavior of the ternary blends.

sonable miscibility, good mechanical properties, and high loss factor over a wide temperature range could be obtained using suitable compositions of medium chlorine content amorphous CPEs. To investigate the effect of ENR on the properties of the PVC/CPE/ENR blends, the amount of ENR was varied as shown in Table IV. CPE H-135 was chosen based on the results of the previous section. It can be seen from Figure 4 that as the amount of ENR 50 increases, the splitting of the two peaks becomes less significant and is gradually diminished. However, about 20 phr of ENR 50 seems to be a suitable amount to be used because a good balance of mechanical properties with reasonably high loss factor over a wide temperature range was obtained. On the other hand, at least under the present experimental conditions, blends using ENR 25 (15 and 16) gave triple peaks, indicating poor miscibility (Fig. 5) with relatively poor mechanical properties. PVC/ENR25 blends have been observed to give only partial or limited miscibility.[17]

Table IV Recipes[a] (phr) and Properties of PVC/CPE/ENR Blends

	10	11	12	13	14	15	16
PVC	50	44.5	40	33.3	25	33.3	33.3
CPE H-135	50	44.5	40	33.3	25	33.3	33.3
ENR 50		11	20	33.3	50	20	
ENR 25						13.3	33.3
M100 (MPa)	8.1	8.3	7.6	5.4	2.3	4.5	1.3
TS (MPa)	12.6	11.2	12.8	14.2	11.4	7.4	2.8
EB (%)	265	265	430	620	1020	330	285
Hardness							
JIS A	94	97	97	94	81	90	66
Shore D	50	55	55	50	32	42	20

[a] Plus #8813 (0.5 phr), and AC-6A (0.7 phr).

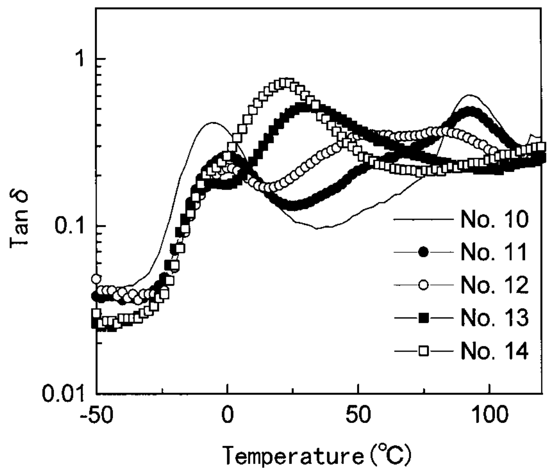

Figure 4 The effect of ENR 50 on the tan delta behavior of the ternary blends.

Filled Ternary Blends

Some trials were carried out to find the appropriate composition for the PVC/CPE/ENR blends that were subsequently used as the starting formulation for preparing filled systems. A PVC/CPE/ENR ratio of 23.3 : 56.7 : 20 was chosen and various fillers were investigated. The recipes and type of fillers used are shown in Table V. The damping behavior, as represented by the loss factor at 20°C, was measured over a frequency range of 100–1000 Hz. Generally, the damping factor η of polymer-laminated steel[18] is given by the following equation:

$$\eta = 14\eta m(E_m/E_s)(H_m/H_s)2$$

for $E_m/E_s \ll 1$, where η_m is the loss factor of the viscoelastic material, E_m is the elastic modulus of the viscoelastic material, E_s is the elastic modulus of the steel, H_m is the thickness of the viscoelastic material, and H_s is the thickness of the steel.

The equation suggests that large η can be obtained when a viscoelastic material has a high loss factor and elastic modulus. However, over the entire range of frequencies studied, recipes 19 and 20 show significantly higher loss factor than the others in spite of their comparable elastic modulus as indicated by the hardness data. Regardless of the particle size, it is noticeable from these results that flake-shaped fillers are more operative in improving the damping properties of polymer-laminated steel. This is supported by the fact that the mica (flake type) has a bigger particle size than the silica and the Crown clay (gran-

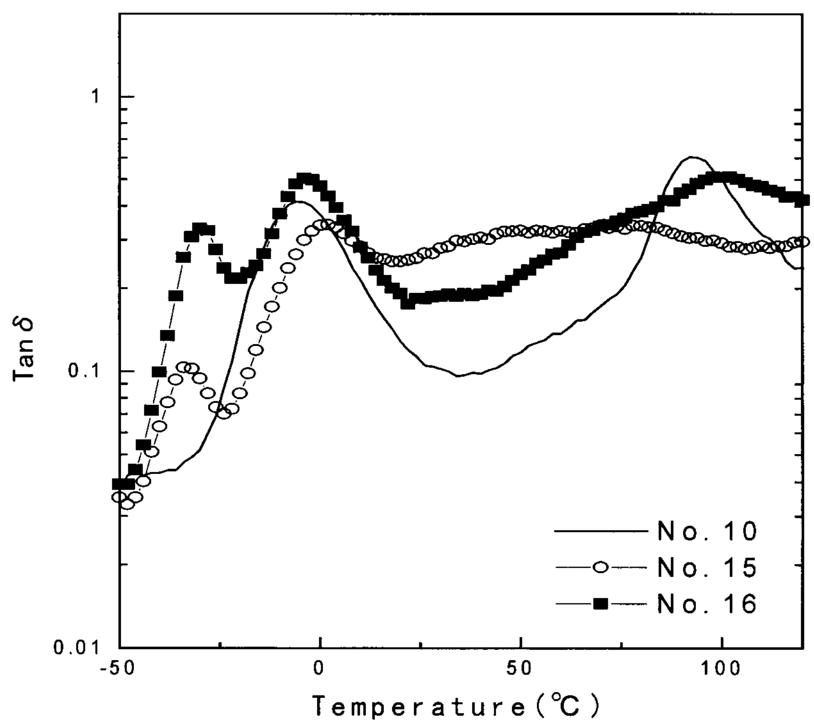

Figure 5 The effect of ENR 25 on the tan delta behavior of the ternary blends.

Table V Mechanical Properties and Damping Behavior of PVC/CPE H-135/ENR Ternary Blends[a] Containing Various Fillers

	Fillers					
	17	18	19	20	21	22
	Unfilled	Crown Clay	Burgess Clay	Phlogopite Mica	Hydrous Silica	Carbon Black
M100 (MPa)	3.2	13.3	12.8	9.1	13.4	14.5
TS (MPa)	11.2	14.3	15.1	11.2	19.0	17.9
E_m (%)	555	135	115	30	235	210
H_s (JIS A)	78	96	94	95	96	97
Loss Factor at 20°C						
100 Hz	0.01	0.08	0.08	0.10	0.02	0.06
250 Hz	0.02	0.10	0.14	0.12	0.05	0.06
500 Hz	0.02	0.12	0.18	0.15	0.07	0.08
1000 Hz	0.03	0.14	0.21	0.19	0.08	0.10

E_m, elongation at maximum strength.
[a] At 23.3 : 56.7 : 20 ratio, 100 phr filler, plus KS-42B6 (1 phr) and AC-6A (0.7 phr).

ular type). Those flake-type fillers just absorb the given energy by the friction of those plates.[19] Subsequently, various types of flake-shaped fillers were evaluated to determine their effect on the damping properties. The recipes are shown in Table VI in which 20 phr of Coumarone resin was included.

Our more comprehensive and systematic study on the effect of various resins such as Coumarone on the damping behavior of the filled blends is in progress and will be reported in the near future. The loss factor of each recipe at 20°C over the entire range of frequency investigated was quite consistent and higher than those of granular filler-filled recipes. For recipes 20 and 23, it is demonstrated in Figure 6 that the tan δ was quite consistent from 0 to 100°C and higher than the

Table VI Mechanical Properties and Damping Behavior of PVC/CPE H-135/ENR Ternary Blends[a] Containing Various Shape Fillers

	23	24	25	26	27
			Wollastonite		
NYAD 325	Phlogopite Mica	Muscovite Mica	NYAD 325	NYAD 400	Graphite CP-2
M100 (MPa)	8.7	7.2	4.6	5.2	12.8
TS (MPa)	8.8	7.6	7.5	7.8	13.9
E_m (%)	180	34	380	370	55
JIS A	96	97	92	94	96
Shore D	59	59	50	51	57
Loss Factor at 20°C					
100 Hz	0.14	0.17	0.12	0.10	0.15
250 Hz	0.15	0.18	0.13	0.11	0.17
500 Hz	0.17	0.19	0.14	0.12	0.19
1000 Hz	0.18	0.20	0.15	0.13	0.19

[a] At 23.3 : 56.7 : 20 ratio, 100 phr filler, Coumarone resin (20 phr), KS-42B6 (1 phr), and AC-6A (0.7 phr).

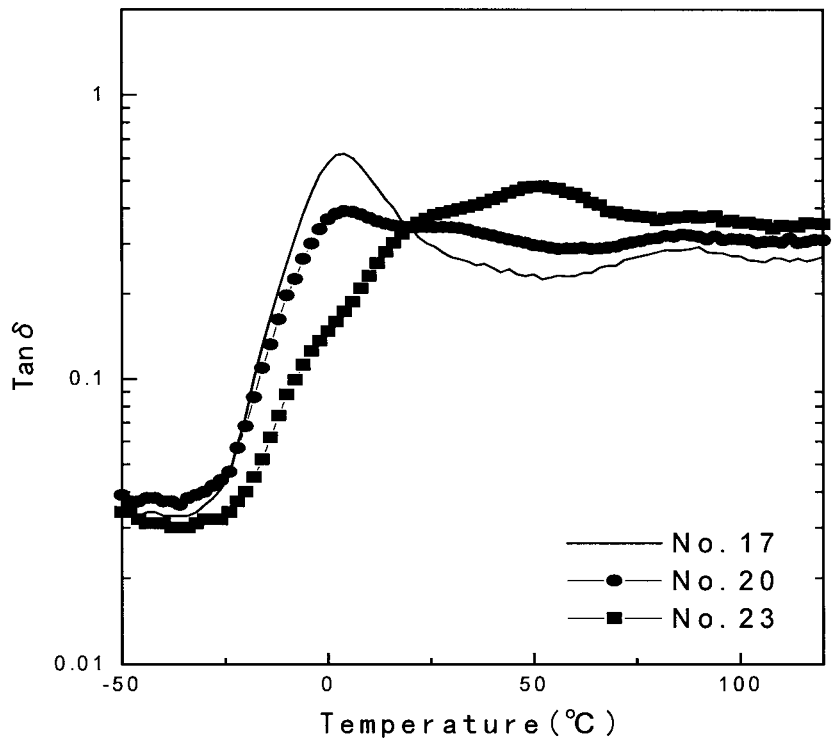

Figure 6 The effect of flake-shape fillers on the tan delta behavior.

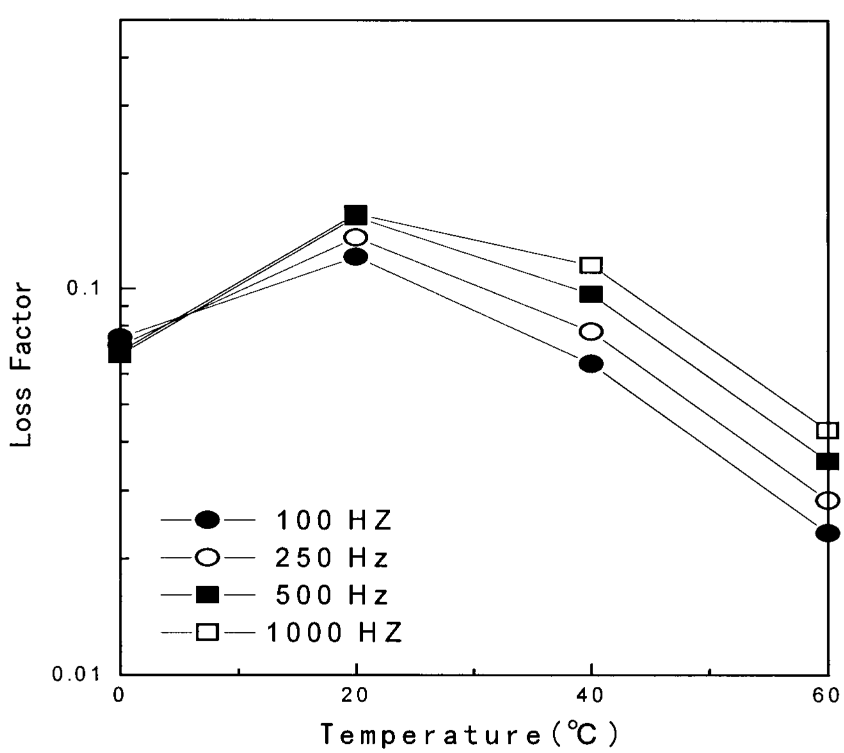

Figure 7 The loss factor behavior of mica-filled PVC/CPE/ENR blend.

values obtained for the unfilled system (17). Based on the laminated steel testing, recipe 23 shows high tan δ values from 0 to 40°C under varying frequencies (Fig. 7).

CONCLUSION

Several compositions of PVC/CPE/ENR blends using various types of CPEs, ENR 25, and ENR 50 were evaluated. The results indicate that some compositions using amorphous medium chlorine content CPE and ENR 50 could be obtained to give good miscibility, mechanical properties, and damping behavior suitable for a high-performance vibration absorber. Furthermore, flake-shaped fillers could be utilized to improve the damping behavior of the PVC/CPE/ENR blends.

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