

Damping Characteristics of Chlorobutyl Rubber/Poly(ethyl acrylate)/Piezoelectric Ceramic/Carbon Black Composites

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ABSTRACT: In this study, a new kind of damping composite consisting of chlorobutyl rubber, poly(ethyl acrylate), piezoelectric ceramic (PZT), and carbon black (CB) was prepared, and some efforts were made to characterize the damping behavior and explore the damping mechanism. The damping behaviors of the composites were mainly decided by the contents of CB and PZT. When an external vibration was exerted on the composites, the mechanical energy of vibration was transformed into electric energy by PZT; if the resistance was adjusted to a suitable range by the variation of the CB content, the composites could behave as semiconductors: the electric energy could

not be transferred to the surface of the material but rather was dissipated as thermal energy. For this system, when the contents of CB and PZT were between 10 and 30 vol %, respectively, the volume resistivity was between 10^5 and $10^{9.5}$ Ω cm, and a good damping performance could be achieved. On the basis of the results, a theoretical model is proposed to explain the damping performance of the composites. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3670–3676, 2008

Key words: composites; elastomers; fillers; functionalization of polymers; matrix

INTRODUCTION

The control of vibration and noise pollution has become an urgent task in modern society. For this purpose, developing a new style of damping material and researching the damping mechanism are strongly required. Currently, polymers are often used as damping materials because of their viscoelasticity, but they also have some disadvantages. First of all, the damping range of homopolymers is generally 20–30°C because of their narrow glass-transition region, which is not broad enough for practical applications. Second, damping materials derived from polymers often exhibit a strong dependence on the temperature or frequency, and they hardly keep an even damping property in their functional area. A lot of methods, such as polymer blends, interpenetrating networks, and copolymers,^{1–5} have been successfully developed to broaden the effective damping range of polymers and to modify the dependence of damping behaviors on the temperature and frequency. However, there are few results yet that can broaden the transition peaks and at the same time retain a high loss factor. Recently, some studies have been carried out on piezoelectric composite materials^{6–12} and on organic hybrids consisting of

polymers and small molecules.^{13,14} As far as organic hybrids are concerned, the weakness of the intermolecular hydrogen bond can easily lead to phase separation during the application process, which limits their usage in long-term service, whereas piezoelectric composite materials do not have such a disadvantage.

Piezoelectric ceramic (PZT) is a kind of material that has the ability to transform vibration and noise into electric energy. If PZT is pressed or pulled in a specific direction, a positive electrical charge or a negative one, respectively, will appear on the surfaces, and the electrical charge density has a proportional relationship with the stress intensity; this is called the piezoelectric effect. However, the hard and crisp properties of PZT limit its applications. Fortunately, Newnham et al.¹⁵ in 1978 put forward a novel idea for a piezoelectric composite. According to the approach, PZT and flexible polymers are mixed with each other by certain combination methods to obtain a piezoelectric composite with a certain mass ratio and a certain space distribution to take advantage of the two kinds of materials, which compensate each other and have good synthesis properties. As a new kind of damping material, a piezoelectric composite overcomes the weakness that properties of polymers heavily depend on the temperature and frequency and avoids the disadvantage that PZT is hard, frail, and not easily processed, preserving the advantages of the two materials.

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Research on the relation between the damping property and electric resistance shows that a certain matched electric resistance is necessary for a piezoelectric composite to have a high damping property.¹⁶ Therefore, it is possible to control the damping property of piezoelectric composites by changes in the quantity of carbon black (CB).^{17,18}

In our previous study,¹⁹ poly(ethyl acrylate) (PEA) was used to successfully broaden the effective damping region of chlorobutyl rubber (CIIR) to the room-temperature region, but it was found that the loss factor of CIIR/PEA blends was not high enough and, moreover, its dependence on temperature (or frequency) was not completely overcome either. In this work, to enhance the damping property of CIIR/PEA blends, PZT and CB were added to prepare CIIR/PEA/PZT/CB composites, and the effect of the PZT and CB contents on the damping property of piezoelectric composites was studied intensively.

EXPERIMENTAL

Materials and preparation

CIIR (Exxon 1068), with a Mooney viscosity and chlorination concentration of $ML_{1+4}(125^{\circ}\text{C}) = 45\text{--}55$ and 1.1–1.3 wt %, respectively, was produced by U.S. Exxon Co. (Supplied by Exxonmobil Chemical Services Co., Ltd., Shanghai, China) PZT was supplied by Shandong Guoteng Functional Ceramic Co., Ltd. (Dongying, Shandong, China). PEA was synthesized by emulsion polymerization with a $\text{K}_2\text{S}_2\text{O}_8\text{--FeSO}_4$ redox initiator system at a temperature of $25 \pm 2^{\circ}\text{C}$. When the reaction was finished, PEA was obtained by the breaking of the emulsion, coacervation, and drying. Phenol–formaldehyde resin (PR201), which was used as the cocuring agent of CIIR and PEA, was offered by Chongqing Resin Plant of China (Chongqing, China). Other chemicals, such as ZnO, MgO, CB, and stearic acid, were commercially available.

PZT with alcohol was lapped in a ball mill to be shattered for 48 h and then was cooled and kept at room temperature for 24 h. After most of the alcohol spontaneously vaporized, PZT was sieved through a net of 400 eyes, and this was followed by vacuum drying. PEA was blended with CIIR in a ratio of 30/70 (wt %) by a twin-roll mill for 20 min at 160°C . After cooling, PZT, CB, PR201, and other accelerating agents were added at room temperature. The resulting blends were then vulcanized at 160°C under a pressure of 10 MPa for 20 min. The vulcanized sheets were directly cut into certain pieces for the analysis.

Electric resistance test

For the high-electric-resistance sample, the electric resistance was measured with a model ZC36 megger

(Shanghai Precise Scientific Instrument Co., Shanghai, China). For the low-electric-resistance sample, the four-electrode test method was adopted according to the American National Test Standards.

Vibration analysis

The vibration performance of the composites was analyzed with a model 3652 dynamic signal analyzer (Hewlett–Packard Co., USA) as follows:

1. The vulcanized sheets were cut into $60 \times 50 \times 3 \text{ mm}^3$ samples, which were then fixed at one end to an iron stand, and the fixed-frequency knock was exerted through the running of an electric engine. Through a sensor on the dynamic signal analyzer, the vibration decay time of the composites was recorded after the removal of the external force.
2. The vulcanized sheets were cut into $60 \times 16 \times 3 \text{ mm}^3$ samples. Both ends of the samples were fixed on self-made tongs, and a cork ball with a radius of 5 mm was allowed to fall freely from 1 m high down to the middle of the samples; then, the vibration decay time of the samples was measured by a sensor after the cork ball was removed.

RESULTS AND DISCUSSION

Influence of PZT on the damping property of the composites

The piezoelectric composite is a new kind of damping material, whose damping function mainly originates from three parts: the viscoelastic damping of the polymer (α), the friction damping between the polymer and fillers or fillers themselves (β), and the piezoelectric damping of PZT (γ). As for γ , there are two steps of the energy dissipation process, which are shown as follows:



Therefore, the damping property of piezoelectric composites initially depends on the conversion between the mechanical energy and electric energy.

Figures 1 and 2 show the vibration attenuation of the composites with PZT contents of 0 and 30 vol %, respectively, under the condition of the cork ball bumping. From a comparison of Figures 1 and 2, it is evident that with the 10 vol % content of CB unchanged, the vibration attenuation time of the

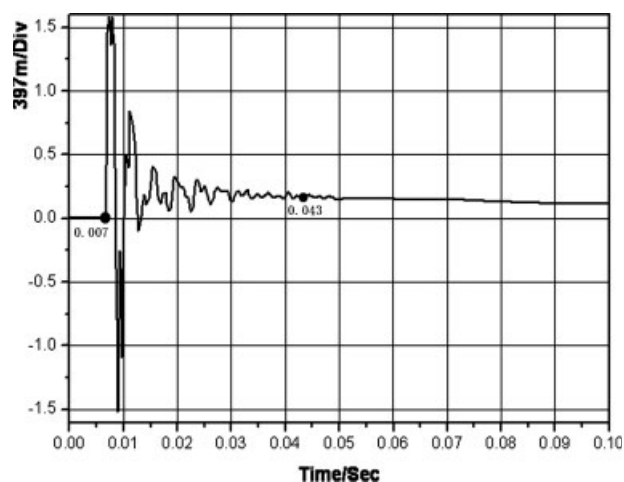


Figure 1 Attenuation time of the sample with 10 vol % CB and without PZT.

sample with 30 vol % PZT was shorter than that of the other sample without PZT. Therefore, adding the proper amount of PZT can decrease the vibration attenuation time and improve the damping property of piezoelectric composites.

Figures 3 and 4 show the influence of the PZT content on the attenuation time of the composites knocked at a certain frequency and with a cork ball, respectively. It can be observed in both Figures 3 and 4 that with increasing PZT, the attenuation time of the composites shows a trend of descending initially but rising subsequently and exhibits a minimum at a PZT content of 30 vol %. The reason can be expressed as follows: as the content of PZT increases, PZT and CB will match better and better, and γ and β rise, although α decreases, and $\Delta\alpha$ is smaller than $\Delta\beta + \Delta\gamma$. Consequently, the integrated damping ($\alpha + \beta + \gamma$) goes up, and at the point of

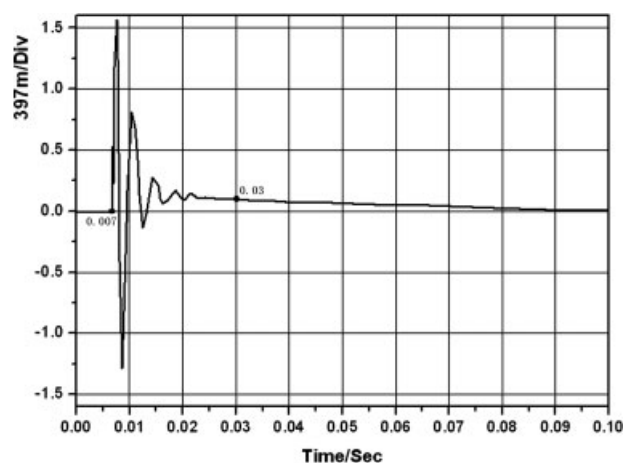


Figure 2 Attenuation time of the sample with 10 vol % CB and 30 vol % PZT.

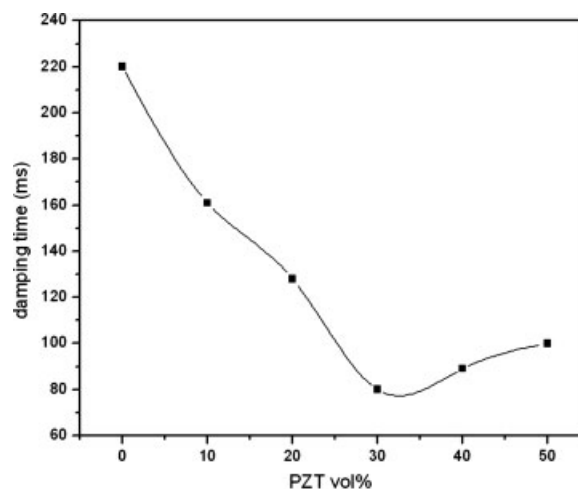


Figure 3 Influence of the PZT content on the damping time of composites with 10 vol % CB under a knocking frequency of 50 Hz.

30 vol % PZT, the piezoelectric composite attains the highest value. With the content of PZT further growing, β keeps on going up; however, because the content of CB is constant, the increase of γ is limited, whereas α descends much at the same time. In other words, $\Delta\alpha$ is much bigger than $\Delta\beta + \Delta\gamma$. As a result, $\alpha + \beta + \gamma$ drops, whereas the attenuation time increases. On the other hand, too much PZT will result in excessive cost (because of its high price) and a reduction of the mechanical properties of piezoelectric composites because the material becomes too hard and crisp. Therefore, 30 vol % PZT is very condign.

In addition, the PZT particles also have a certain influence on the volume resistivity of the composites, as shown in Figure 5. Under the same condition of 10 vol % CB, with an increase in PZT, the volume

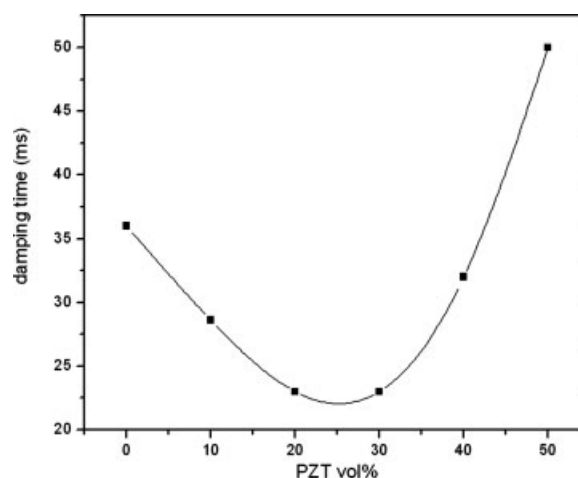


Figure 4 Influence of the PZT content on the damping time of composites with 10 vol % CB during knocking with a cork ball.

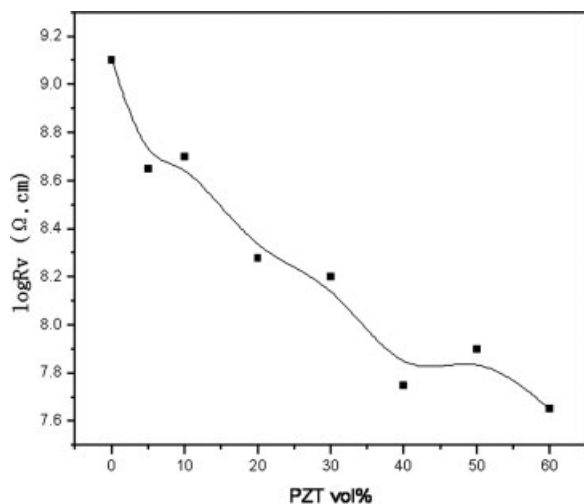


Figure 5 Change of the volume resistivity (R_v) of piezoelectric composites with the PZT content varying from 0 to 60 vol % and with CB remaining at 10 vol %.

resistivity of the composites goes down. However, the trend of the volume resistivity, which decreases lentamente with increasing PZT, is different from that with increasing CB (as shown later in Fig. 10). This is because PZT is a kind of semiconductor, and its conduction property is better than that of a rubber matrix but poorer than that of CB.

Influence of CB on the damping property of the composites

As mentioned previously, the second step of energy dissipation in the piezoelectric composite is the electric energy/thermal energy conversion, for which CB, as a primary electric filler in the composite whose dosage is directly related to the conductivity

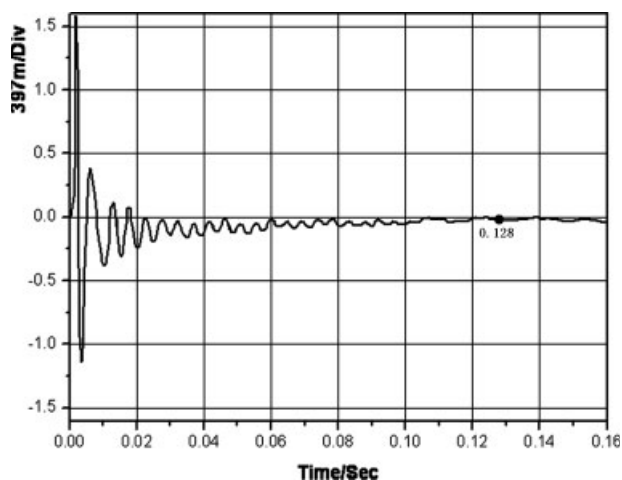


Figure 6 Attenuation time of a sample with 40 vol % PZT and without CB.

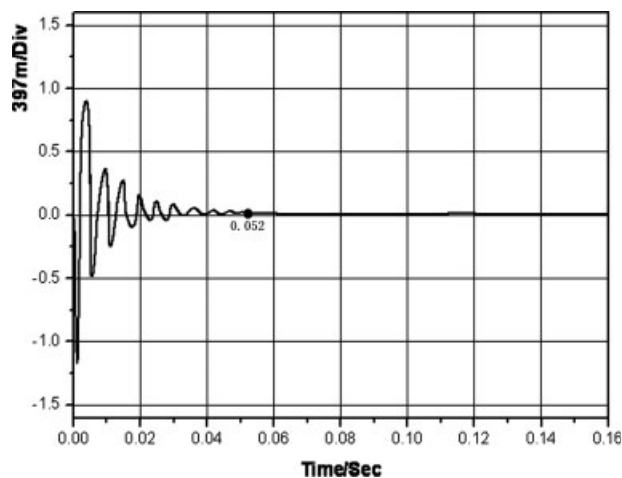


Figure 7 Attenuation time of a sample with 40 vol % PZT and 15 vol % CB.

and conversion of electric power, is one of the most important factors that affect the damping property.

Figures 6 and 7 show the vibration attenuation of the composites with CB contents of 0 and 15 vol %, respectively, under the condition of the cork ball bumping. From a comparison of Figures 6 and 7, it can be seen that with 40 vol % PZT kept constant, the vibration attenuation time of the sample with 15 vol % CB is evidently shorter than that of the sample without CB. Therefore, it is clear that adding an opportune content of CB can decrease the vibration attenuation time of the piezoelectric composite and improve its damping property. Figures 8 and 9 indicate the influence of the CB content on the attenuation time of the samples knocked with a certain frequency or a cork ball. With increasing CB, the

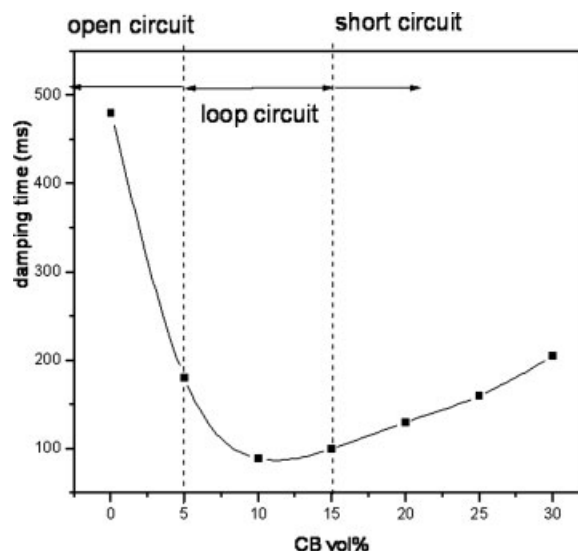


Figure 8 Influence of the CB content on the attenuation time of composites with 40 vol % PZT under a knocking frequency of 50 Hz.

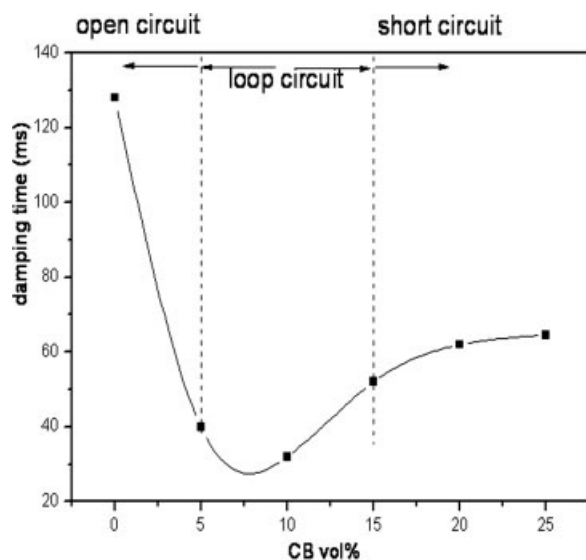


Figure 9 Influence of the CB content on the attenuation time of composites with 40 vol % PZT during knocking with a cork ball.

attenuation time decreases first but rises afterward, and a minimum valley around 10 vol % CB can be observed. When the CB and PZT particles are mixed together in the matrix, they are made of small loops; only when the volume resistivity of the composite is appropriate can every small loop become a power-wasting unit, and so it can function as the conversion unit from electric energy to thermal energy. Therefore, for these systems, with 10 vol % CB, CB and PZT particles get in touch with each other and form conducting electric networks with appropriate electric resistance, by which the electric energy can be converted to thermal energy.

To understand the effect of the CB content on the attenuation time of piezoelectric composites, the relation between the CB content and electrical resistivity has been investigated, as shown in Figure 10. It is obvious that the electrical resistivity displays a declining trend with increasing CB. At the beginning, because the content of CB is small, its particles are scattered in the composite, and the electric network does not form yet; thus, the piezoelectric composite is in the situation of an opening circuit, and the volume resistivity is relatively high and shows a slight decrement with increasing CB loading. When the CB content goes up to 5 vol %, the volume resistivity decreases slowly; at a certain time when CB reaches one certain critical density (10 vol % or so), fillers form electric networks at the moment, and the mass resistivity goes down rapidly. When the content of CB varies from 5 to 15 vol %, filler particles come into contact with one another, and they induce the galvanic circle ultimately. Beyond 15 vol % CB, although the density of electric networks becomes

bigger, a further increase in CB can raise the conductivity only slightly for it exceeds the threshold. Therefore, the electric resistivity can be controlled through changes in the volume content of CB, which is a valid method to raise the power-wasting ability and the damping property.

If R denotes the electric resistance of the composite, C denotes the capacitance of PZT, and ω denotes the vibration frequency, then $R = 1/\omega C$ is the best matching condition for the composite. Connecting Figures 8–10, we can see that when the content of the CB is between 5 and 15 vol %, the vibration attenuation time is shorter. Under this circumstance, the value of the logarithm of the volume resistivity is 2.5–9.5, so the matching mass resistivity of the composite is $10^{2.5}$ – $10^{9.5}$ Ω cm. This scope, including the critical point of varying mass resistivity, is the most changeable district.

Theoretical model for the piezoelectric composites

To gain insight into the damping mechanism of piezoelectric composites, a theoretical model is brought forward according to the experimental results. As the scheme of Figure 11 shows, when a sample is subjected to fixed-frequency knock, the combination damping property ($\alpha + \beta + \gamma$) of the material climbs up to a maximum but slides down along with CB increasing.

If a composite does not contain CB, only α and a small amount of β contribute to the damping function (from PZT, ZnO, etc.). PZT in the composite can transform mechanical energy into electric power but

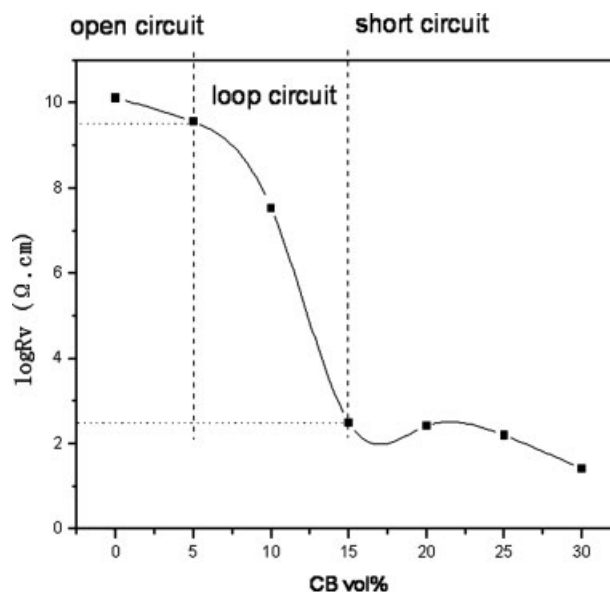


Figure 10 Change of the volume resistivity (R_v) of piezoelectric composites with the CB content varying from 0 to 30 vol % and with PZT remaining at 40 vol %.

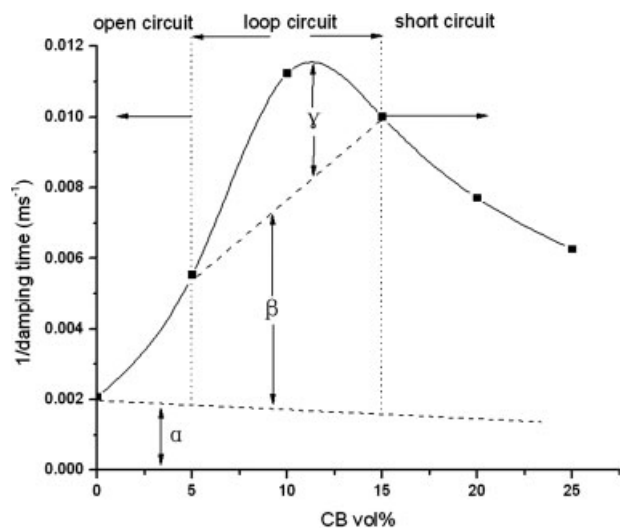


Figure 11 Schematic representation of the effect of CB on the volume resistivity and damping performance of the composites.

cannot implement the conversion between electric power and heat energy because it lacks the function of a conductive body; consequently, the system has no γ . When the CB density is lower than 5 vol %, the matrix and fillers cannot contact each other well, and this leads to its poor conductance, as shown in Figure 12(a). Under this circumstance, the piezoelectric composite behaves like an open circuit, so electric energy also cannot be transported into the matrix and thus cannot be converted into the thermal energy well; as a result, it can be saved only in the PZT particles, which obstruct the conversion between electric energy and thermal energy. Hence, as the CB content varies from 0 to 5 vol %, α goes down gradually, β goes up, and γ can be neglected. As a result, an increasing trend of $\alpha + \beta + \gamma$ can be observed.

As CB rises above 5 vol %, the filler particles gradually get in touch with each other, leading to the formation of the electric networks, as shown in Figure 12(b). Like metallic networks, these electric networks run through the whole polymer matrix and become electric routes to conduct electric energy. At the same time, because of the large electric resistance of the material, the energy cannot be conducted to the surface directly but rather is converted to thermal

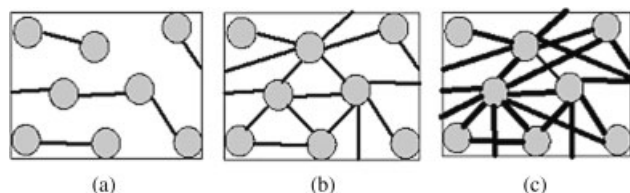


Figure 12 Schematic representations of the circuit models: (a) open circuit, (b) loop circuit, and (c) short circuit.

energy in the composite. Thus, α and β show the same tendency as the former stage, but γ is greatly enhanced.

With a further increase in CB, filler particles come into intimate contact with one another, and the electric network becomes more and more compact, as shown in Figure 12(c); this makes the electric resistance of the composite become smaller and smaller. Therefore, a short circuit in the piezoelectric composite gradually is formed (>15 vol % CB), which can conduct electric energy to the composite surface quickly, it being equal to connect the ground, at which the electric energy cannot be converted into the thermal energy; as a result, γ decreases greatly. At the same time, α goes down and β goes up. As a result, $\alpha + \beta + \gamma$ is depressed from the maximum.

In a word, by the variation of the CB content, the composite can transform from an open circuit to a loop circuit to a short circuit; and within the scope of the loop circuit, the piezoelectric composite can carry out the conversion of mechanical energy to electric energy to thermal energy.

CONCLUSIONS

In this work (for purpose of damping applications), CIIR/PEA/PZT/CB composites were prepared. The results from research on the properties of the composites show that the damping behavior of the composites strongly depends on the contents of CB and PZT, and when the contents of CB and PZT are between 10 and 30 vol %, the volume resistivity of the materials is between 10^5 and $10^{9.5}$ Ω cm, and a good damping performance can be achieved. Therefore, by the adjustment of the electrical resistance to a suitable range by the variation of the CB content, the composites can behave as semiconductors, in which the electric energy is not transferred to the surface of the material but rather is dissipated as thermal energy. According to the results, a theoretical model based on an open circuit to a loop circuit to a short circuit has been proposed to explain the damping performance of the composites.

References

1. Min, B. G.; Stachurski, Z. H.; Hodgkin, J. H.; Heath, G. R. *Polymer* 1993, 34, 3620.
2. Fay, J. J.; Murphy, C. J.; Thomas, D. A.; Sperling, L. H. *Polym Eng Sci* 1991, 31, 1731.
3. Foster, J. N.; Sperling, L. H. *J Appl Polym Sci* 1987, 33, 2637.
4. Hourston, D. J.; Aughes, I. D. *J Appl Polym Sci* 1977, 21, 3487.
5. Chang, M. C. O.; Thomas, D. A.; Sperling, L. H. *J Polym Sci Part B: Polym Phys* 1988, 26, 1627.
6. Uchino, K.; Ishii, T. *Jpn Ceram Soc Scholarly Pap Mag* 1988, 96, 863.
7. Sumita, M.; Gohda, H.; Asia, S.; Miyasaka, K.; Fukuda, A.; Suzuki, Y.; Utino, K. *Macromol Rapid Commun* 1991, 12, 657.

8. Sumita, M. *Shinsozai* 1993, 4, 66.
9. Asai, S.; Nakashima, M.; Sumita, M.; Kaneko, H.; Kaneko, I.; Ohhira, Y.; Hori, M. *J Mater Sci Jpn* 1997, 34, 244.
10. Sumita, M. *Koubunshi* 1997, 46, 116.
11. Sumita, M. *Funct Mater* 1995, 15, 12.
12. Akasaka, S.; Sumita, M.; Date, M.; Tokushima, T. *Meet Polym Mater Forum Text Soc Polym Sci Jpn* 1997, 6, 165.
13. Wu, C. Y.; Qian, S. Y.; Wu, C. F. *J Funct Polym* 2005, 4, 586.
14. Zhou, X. Q.; Wu, C. F. *Chin J Nonferrous Met* 2004, 2, 232.
15. Newnham, R. E.; Schembeim, J. I.; Lee, J. W. *J Intell Mater Syst Struct* 1993, 7, 289.
16. Hagood, N. W.; Flotow, A. von. *J Sound Vibr* 1991, 146, 243.
17. Sumita, M.; Gohda, H.; Asai, S.; Miyasaka, K.; Furuta, A.; Suzuki, Y.; Uchino, K. *Macromol Rapid Commun* 1991, 12, 657.
18. Hori, M.; Aoki, T.; Ohira, Y.; Yano, S. *Compos A* 2001, 32, 287.
19. He, X. R.; Huang, G. S.; Wang, J. H. *China Synth Rubber Ind* 2005, 28, 44.