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Influence of aspect ratio and skin effect on EMI shielding of coating materials fabricated with carbon nanofiber/PVDF

B. O. LEE, W. J. WOO, H. S. PARK, H. S. HAHM, J. P. WU, M. S. KIM*
Division of Ceramic and Chemical Engineering, Myongji University,
San 38-2 Namdong, Yongin, Kyunggido 449-728, Korea
E-mail: myungkim@mju.ac.kr

The effectiveness of electromagnetic interference (EMI) shielding was measured for poly vinylidene fluoride (PVDF) coating materials containing carbon nanofibers. Carbon nanofibers produced from the C_2H_4/NC73 system exhibited higher shielding effectiveness (SE) by relatively large specific surface area and high aspect ratio than those from others. When the thickness of carbon nanofibers filled PVDF coating materials varied from 25 to 50 μm, the electrical conductivity of coating materials increased sharply from 1.34 to 1.91 S/cm. However, the electrical conductivity approached a certain value with further raise of the thickness. This phenomenon denotes that a critical thickness of coating materials exists around 50 μm. The electrical conductivity and SE of coating materials decreased dramatically as the carbon nanofiber fillers were milled. It could be concluded that the decrease of the shielding effectiveness of carbon nanofiber filled composite was due to the decrease of the filler's aspect ratio by ball milling. © *2002 Kluwer Academic Publishers*

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1. Introduction

In recent years, the progress of technology has led to an extensive increase in the amount of sophisticated electronic equipments. However, the electromagnetic waves produced from the electronic equipments have adversely effect on the performance of the other equipments. Therefore, an electrically conductive housing is needed to shield electromagnetic interference (EMI) produced from the electronic equipments. The shield should be highly conducting and thus metal is usually used. Metallic housing fabricated with steel, copper, aluminum, etc., were used by surrounding high EMI emitters for shielding. As commercial, military, and scientific electronic devices and communication instruments are used widely, there is an increased interest in shielding against electromagnetic radiation. The lifetime and efficiency of electronic devices and electrical equipments can be increased by the effective EMI shielding. It is well known that high conducting materials like typical metals are well suited for many EMI shielding applications [1, 2]. However, since shields fabricated with metals have shortcomings of heavy weight, corrosion, and physical rigidity, the electronics industry has resorted to metallized plating on plastics. Further efforts by the electronics industry to develop more dependable light weight materials for EMI shielding has led to electrically conductive component-filled plastic composites [3–6]. It was anticipated that intricate shapes could be molded from the composite materials by conventional means, yielding a finished part that promised to be more economic and dependable than metal or metal-coated plastics.

The principle factor influencing the performance of conductive component-filled plastic composites is the aspect ratio of the conductive fillers [7–10]. The aspect ratio is defined as the ratio of the length to the diameter of the conductive fillers. According to the electromagnetic wave percolation theory, if the conductive filler in the plastic retains a high aspect ratio, the filler easily forms a conductive network and the critical concentration of the conductive filler required to achieve the EMI shielding effect is low. At a certain threshold value of volume fraction of the filler, the particles or fibers are sufficiently close-packed to form unbroken conducting pathway through the composite, and the conductivity of the material increases sharply. A way of maximizing the conductivity would be to control the arrangement of the filler particles such that percolating networks form at a relatively low volume fraction [9]. A process for fabricating EMI shielding is progressed by blending and mixing a composition including resin binder and filler.

Carbon nanofibers are noble materials which can be produced by the decomposition of carbon containing gas over certain metal particles [11]. The diameter of carbon nanofiber is governed by that of catalyst particle responsible for its growth. Carbon nanofibers with high aspect ratio have advantages in both electrical

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[*] Author to whom all correspondence should be addressed.

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conductivity and specific surface area, so their SE is superior to general carbon fiber and carbon black. In this study, carbon nanofibers prepared by chemical vapor deposition of hydrocarbons with nickel-copper bimetallic catalysts were used as the conductive fillers.

The frequency permeability of composite materials has been studied theoretically and experimentally on a variety of materials [12, 13]. In particular, it was deduced that, for composites made of a dispersion of carbon nanofibers particles in a matrix, the skin effect could drastically affect the measured permeability. When the coating layer thickness is not deep compared to the skin depth at a given frequency, the measured permeability is affected by the skin effect [14–16]. Electromagnetic radiation at high frequencies penetrates only the near surface region of an electrical conductor. The electric field of a plane wave penetrating a conductor drops exponentially with increasing depth into the conductor [17]. The depth at which the field drops to 1/e of the incident value is called the skin depth (δ) and it is given by $\delta = (2/f\mu\sigma)^{1/2}$, where $f =$ frequency, $\mu =$ permeability, and $\sigma =$ bulk material conductivity. Hence, the skin depth decreases with increasing frequency, conductivity or permeability.

The frequency permeability of composite materials containing conducting carbon nanofibers was investigated in the range of 500 MHz ~ 1.5 GHz frequency. The objective of this study is to investigate the influence of aspect ratio and skin effect on the EMI shielding effectiveness with carbon nanofiber filled PVDF composites.

2. Experimental procedure

Carbon nonofibers with the diameters ranging 50–200 nm were prepared from the decomposition of propane, ethylene and acetylene gas over nickel-copper and pure nickel catalysts. The powder catalysts were prepared by co-precipitation of the metal carbonates from mixed nitrate solutions using ammonium bicarbonate. The PVDF solutions were made by stirring the mixture containing 7–10 wt% of PVDF and 90–93 wt% of N-methyl-2-pyrrolidone (NMP) at 60°C for at least 30 min. Carbon nanofibers or carbon blacks were crushed in a mechanical mixer and ball mill. The crushed fillers (40 wt% of PVDF) were introduced into the PVDF solution, and the mixture was stirred at 600 rpm for 30 min by a mechanical stirrer and at 20,000–40,000 rpm for 3 min by a homogenizer continuously. The mixture obtained was coated into the size of 15 by 30 cm with the thickness of 180–900 μm using an applicator. The thickness of coating materials reduced to 25–100 μm after drying. The electrical conductivity of coating materials was measured using a digital multi-meter (Keithley 236). The SE of the coating materials was measured using a HP-8720C apparatus according to the method described in ASTM D 4935. BET surface area measurements were carried out using nitrogen adsorption at −196°C.

3. Results and discussion

In order to compare the effectiveness of EMI shielding with different structure of carbon fillers, various carbon nanofibers were prepared from the decomposition of propane, ethylene and acetylene gas over nickel : copper 7 : 3 bimetallic (NC73) and pure nickel (N) catalysts. The carbon nanofibers obtained and a commercial carbon black were used as the fillers to fabricate PVDF composite coatings. Fig. 1 represents the SE of carbon nanofibers and carbon black filled PVDF coating materials. The carbon nanofibers prepared from propane consisted mostly of linear conformation and those from ethylene had mainly twisted conformation. The carbon nanofibers from acetylene had both twisted and helical conformation. It was reported that the carbon nanofibers with coiled or helical conformation were effective filler for EMI shielding [18]. Carbon nanofibers produced from the nickel-copper catalyst had relatively high specific surface areas compared with those from pure nickel catalyst. In order to apply carbon nanofibers as an EMI shielding materials, large specific surface area and high aspect ratio are desirable. As shown in Fig. 1, since carbon nanofibers produced from the C_2H_4/NC73 system had higher SE than those from others, thus further experiments were performed with the carbon nanofibers from C_2H_4/NC73 system.

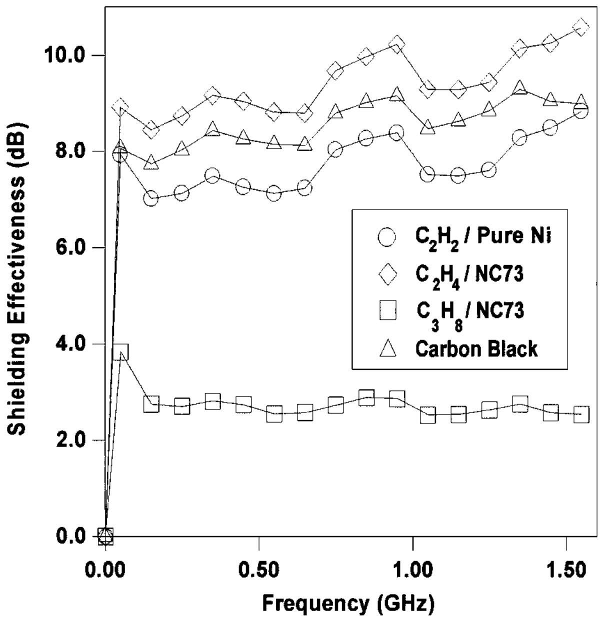


Figure 1 Variation of shielding effectiveness of carbon nanofibers and carbon black filled PVDF coating materials with heat treatment at 1100°C for 1 hr.

Fig. 2 represents the SE of carbon nanofibers filled PVDF coating materials at various concentration of PVDF solution as a function of the frequency. The SE increased with the PVDF concentration rise up to 9 wt% and then decreased with the further increase of PVDF concentration. It was shown that the concentration of PVDF solution played an important role in improving the inhomogeneous behaviors of a coating material. Maximum SE value of carbon nanofibers filled PVDF coating materials occurred at around the 9 wt% concentration. The lack of SE with the high PVDF concentration of 10 wt% could be explained by the inhomogeneity of composite to form a good continuous network due to high viscosity of matrix and entanglement of carbon nanofibers.

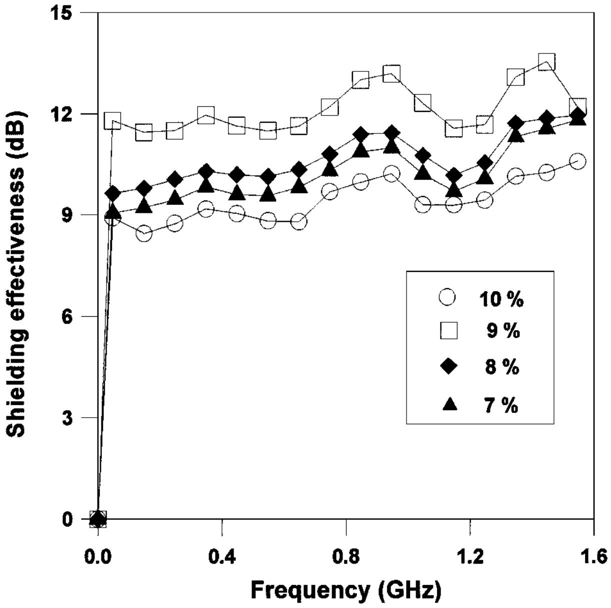


Figure 2 Shielding effectiveness of carbon nanofibers filled PVDF coating materials with different PVDF concentration.

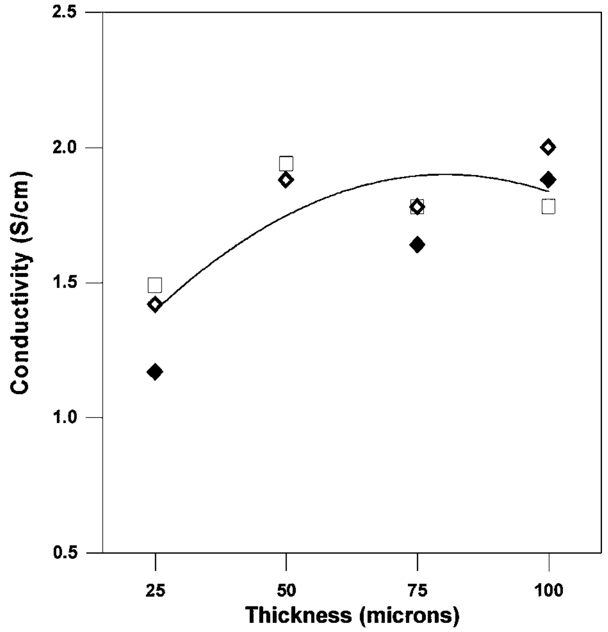


Figure 3 Electrical conductivity of carbon nanofibers filled PVDF coating materials with different thickness.

Fig. 3 represents the variation of the electrical conductivity for a carbon nanofibers filled PVDF coating materials as a function of thickness. When the thickness of carbon nanofibers filled PVDF coating materials varied from 25 to 50 μm, the electrical conductivity of coating materials increased sharply from 1.34 to 1.91 S/cm. However, the electrical conductivity approached a certain value with further raise of the thickness. This phenomenon denotes that a critical thickness of coating materials exists around 50 μm. This behavior is related to the skin effect and it can occur for coating thickness around the skin depth. When the coating layer thickness is less than the skin depth, the measured permeability is affected by the skin effect. Fig. 4 represents the shielding effectiveness of carbon nanofibers filled PVDF coating materials with various coating thickness.

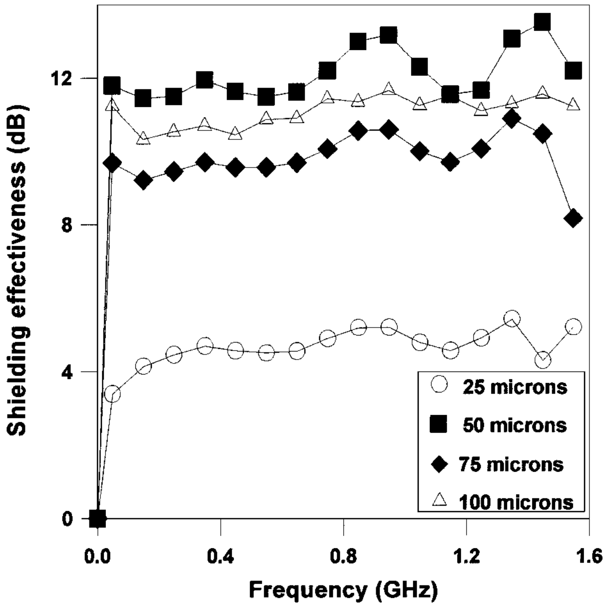


Figure 4 Shielding effectiveness of carbon nanofibers filled PVDF coating materials with different thickness.

The dependence of coating thickness on SE was very similar to that on electrical conductivity of the coating materials.

In order to compare the effectiveness of EMI shielding with the carbon nanofiber fillers having different aspect ratio, the various carbon nanofibers were prepared by mechanical mixing and ball milling. Carbon nanofibers produced from C_2H_4/NC73 were used as the conductive fillers after the heat treatment at 1100°C for 1 hr. Fig. 5 shows SEM micrographs of carbon nanofibers with the different milling conditions. From the SEM image (a), it can be seen that the fibers are twisted conformation and the aspect ratio is relatively high. As crushing condition was getting severe, the shorter carbon nanofibers were observed as shown in Fig. 1b and c.

The electrical conductivity of carbon nanofibers crushed with ball mill and their PVDF coating materials are presented in Table I. With the heat treatment of carbon nanofibers at 1100°C for 1 hr, the electrical conductivity of carbon nanofibers increased by 2.6 times and that of their composite coatings increased by 5.3 times. Although the electrical conductivity of carbon nanofibers was not much changed with ball milling, the electrical conductivity of their composite coatings decreased dramatically. The electrical conductivity of composite coatings decreased to one eighth after 24 hr's ball milling and this phenomenon could be explained by the decreased aspect ratio after ball milling.

Fig. 6 represents the SE of carbon nanofibers filled PVDF coating materials with the different milling conditions. The SE of composite coatings decreased at a similar fashion with the electrical conductivity of them when the carbon nanofibers were crushed by ball mill. From the results, it was concluded that concerning the SE of carbon nanofiber filled composite, the discontinuities developed within the carbon nanofiber network was caused by the decrease of the filler's aspect ratio after ball milling.

TABLE I Electrical conductivities of carbon nanofibers and their PVDF composite coatings with different ball mill treatment of carbon nanofibers

Ball mill treatment of carbon nanofibers	Electrical conductivity of filler at 10000 psi (S/cm)		Electrical conductivity of composite coatings (S/cm)	
	As grown (A)	With heat treatment 1 hr (B)	Filled with (A)	Filled with (B)
None	5.5	14.4	0.6	3.2
Ball mill 1 hr		12.6		1.7
Ball mill 24 hr		13.4		0.4

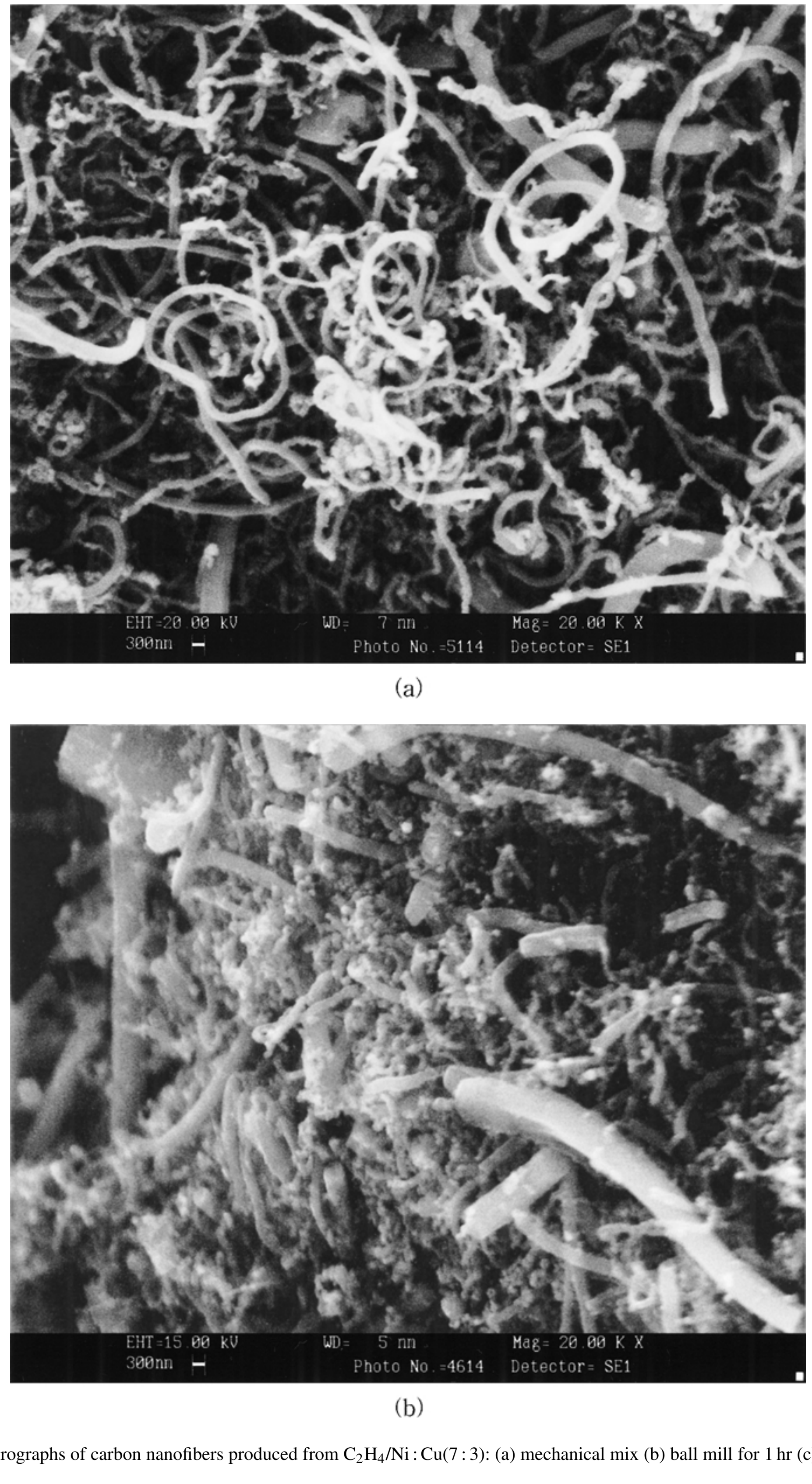
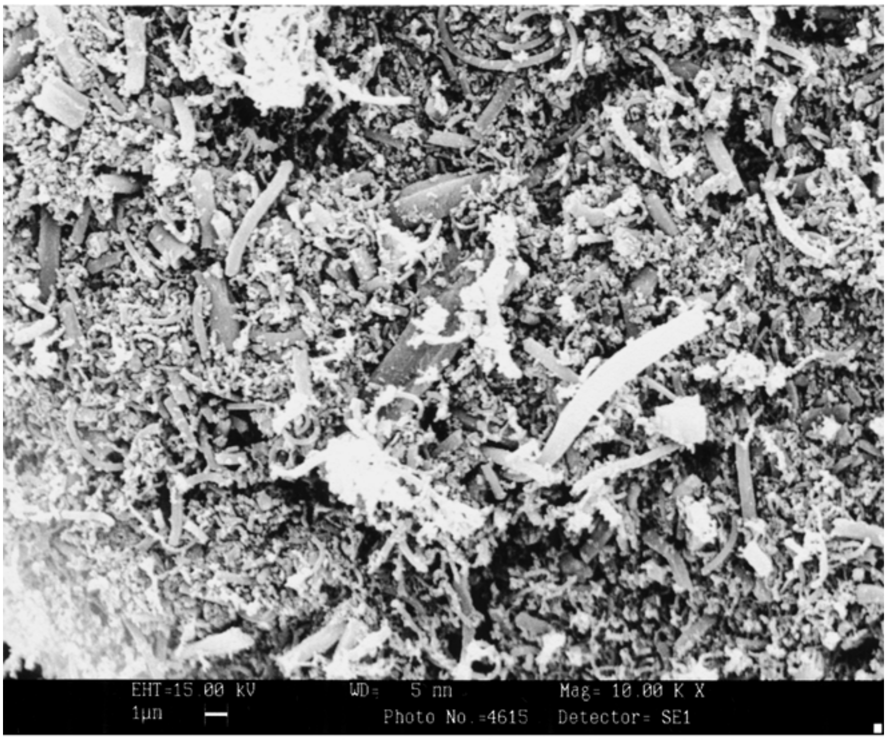


Figure 5 SEM micrographs of carbon nanofibers produced from C_2H_4/Ni : Cu(7 : 3): (a) mechanical mix (b) ball mill for 1 hr (c) ball mill for 24 hr. (*Continued.*)



(c)

Figure 5 (*Continued.*)

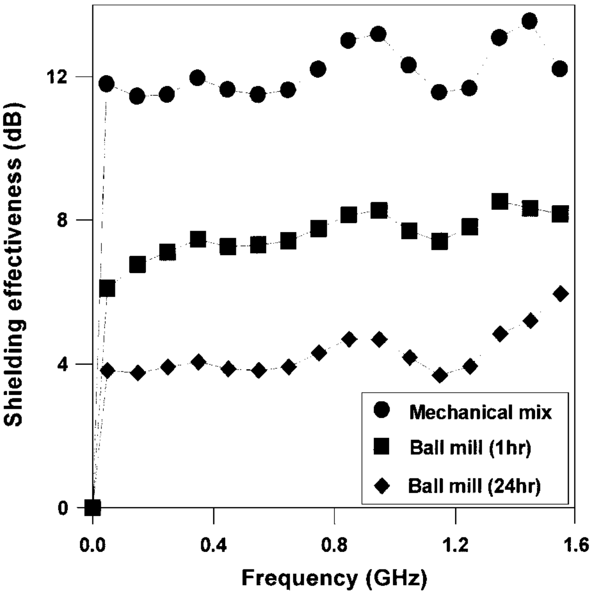


Figure 6 Shielding effectiveness of carbon nanofibers filled PVDF coating materials with different ball mill treatment of carbon nanofibers.

4. Conclusions

Carbon nanofibers were dispersed as conductive fillers in a PVDF matrix and the influence of aspect ratio and skin effect on the SE of resulting composites was investigated. When the thickness of carbon nanofibers filled PVDF coating materials increased from 25 to 50 μm, the electrical conductivity of coating materials increased from 1.34 to 1.91 S/cm, but the electrical conductivity approached a certain value with further raise of the thickness. This phenomenon may indicate that a critical thickness of coating materials exists around 50 μm. The electrical conductivity and shielding effectiveness, SE of coating materials decreased dramatically as the carbon nanofiber fillers were milled. It could be concluded that the decrease of the shielding effectiveness of carbon nanofiber filled composite was due to the decrease of the filler's aspect ratio by ball milling.

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