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Thermal stability of shielding effectiveness of electromagnetic interference of composites

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A series of composites were prepared using polyethylene and various chatter-machined metal fibres (aluminium, copper, steel and brass) and carbon fibre, and the effects of the concentration of the fillers and the thermal treatment of the composites at 80° C in air on the shielding effectiveness (SE) of electromagnetic interference were examined. The order of the generation of SE was, brass > steel > copper ≈ aluminium > carbon. Thermal degradation of SE was scarcely observed in the carbon fibre system and very slightly in the brass and steel systems, while remarkable degradation was observed in the copper and aluminium systems. This degradation was assumed to be due to the formation of an oxidized surface to increase the contact resistance between fillers. Stabilization of the thermal degradation of SE of the aluminium composite was possible to some extent when the aluminium surface was pretreated with certain reagents.

1. Introduction

Recent rapid development of electronic devices such as TV, VTR, OA instruments, medical instruments, computers, etc., has given rise to electromagnetic interference (EMI) because almost all housings of these devices are made of plastics which are transparent to electromagnetic interference. In order to shield the electromagnetic interference, technical approaches have been considered extensively to provide electrically conductive housings, i.e. coating, metallizing and compounding of conductive fillers. Thus, a number of workers have endeavoured to prepare electrical conductive composites, namely electromagnetic interference shielding composites [1–14], and a comprehensive review appeared recently [15].

It is considered that fibrous fillers are superior to other conductive fillers such as powdery particles or flakes, except in economical feasibility [12–15]. However, a new manufacturing process for short-length metal fibre (Chatter Maching) developed by Nakagawa *et al.*, overcame the problem [12–14].

When the development of functional materials such as in this case is desired, electrically conductive composites, durability or life-time of the function of the materials should be taken into consideration. In this paper, therefore, electrically conductive composites were prepared using polyethylene as a matrix, and short-length metal fibres and a carbon fibre, and their thermal stability of electrical conductivity and shielding function of electromagnetic interference as well as generation of these functions, were examined. Furthermore, stabilization of the functions in an aluminium composite system was attempted.

2. Experimental techniques

2.1. Preparation of composites

Commercial powdery high-density polyethylene (HDPE) containing antioxidants (HZ 5305E Product of Mitsui Petroleum Co. Ltd), was used as a matrix. The conductive fillers used were

(i) various types of aluminium fillers: flake (Transmet Co. Ltd, diameter 1.2 ~ 1.5 mm), shaved flake (Mitsui Aluminum Co. Ltd, thickness 50 μm, width 1 mm, length 3 mm), melt-spun short-length fibre (Mitsui Aluminum Co. Ltd, diameter 100 μm, length 3 mm);

(ii) various chatter-machined metal fibres: aluminium, copper, steel and brass (Kobe Chutetsu Co. Ltd, diameter 60 μm, length 3 mm);

(iii) carbon fibre prepared from polyacrylonitrile (Toray Co. Ltd, length 3 mm).

The necessary amount of each filler was thoroughly blended with the powdery HDPE in a polyethylene envelope, and placed between steel plates with a spacer 0.2 cm thick. The blended materials were heated at 130° C for 10 min in air, and then pressed at 130° C under 200 kg cm^{-2} pressure for 5 min to give a 15 cm × 10 cm × 0.2 cm sized composite.

2.2. Measurement of electrical conductivity

The shielding effectiveness (SE) for electromagnetic interference (EMI) can be estimated roughly from the specific resistance of the composites. For measurement of the specific resistance, three samples, 5 cm × 3 cm, were taken from the prepared composites and placed in an apparatus manufactured by our laboratory. The electrical resistances between both ends and one surface of the plaque were measured using the system shown schematically in Fig. 1. The specific resistance was calculated from the following equation.

$$\varrho(\Omega\text{cm}) = \frac{RWT}{L}$$

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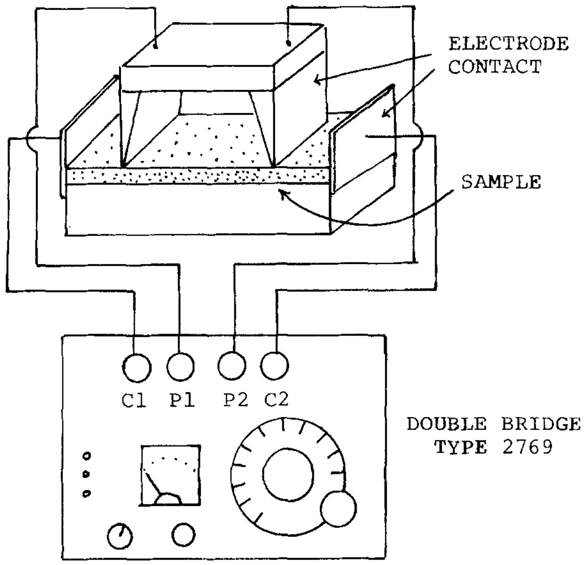


Figure 1 The system for resistance measurement.

where, ϱ is the specific resistance, R the resistance, W the width, T the thickness, and L the length.

2.3. Measurement of shielding effectiveness of electromagnetic interference

In order to estimate real shielding effectiveness (ES) of a material, it is necessary to measure the ratio of the amount of energy passing through the sample to the incident energy. Therefore, a small box in which a pair of antennae were installed, as shown in Fig. 2, was manufactured. At the same time various types of antennae, namely a dipole type, a small dipole type, two kinds of doublet type, a spiral type, two kinds of loop type and a small loop type, were manufactured, and their efficiencies were examined individually. Among them a small dipole-type antenna was found to be reasonably suitable for the estimation of shielding effectiveness of the electric field mode (see Fig. 3) and a small loop antenna for the magnetic field mode (see Fig. 4). Therefore, the shielding effectiveness of the composites for electromagnetic interference was measured using the shielding box installed with a pair of small dipole and a pair of small loop-type antennae, respectively. Three samples, 6 cm × 4 cm, were used for the measurements.

2.4. Thermal treatment

In order to examine changes in electrical conductivity and shielding effectiveness of the composites prepared during the thermal treatment, each sample was heated in air in an electric oven equipped with a fan, or in a vacuum oven at 80° C.

2.5. Treatment of aluminium fillers

In order to prevent the decrease in the shielding effectiveness of aluminium series composites, the catter-machined aluminium fillers were previously treated with the following reagents.

Phosphorous esters (Daihachi Chemical Co. Ltd);

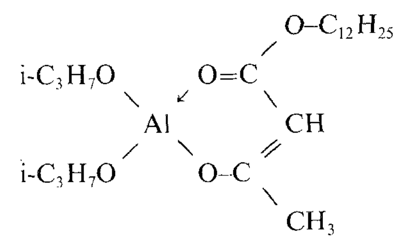
DP-8R : $(HO)P(=O)(OC_8H_{17})_2$

AP-13 : $(HO)P(=O)(OC_{13}H_{27})_2 + (HO)_2P(=O)(OC_{13}H_{27})$

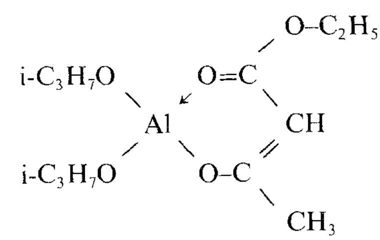
TC-44 : $(C_4H_9)P(=O)(OC_4H_9)_2$

Coupling agents

AL-M (Kawaken fine Chemical Co. Ltd):



ALCH (Kawaken fine Chemical Co. Ltd):



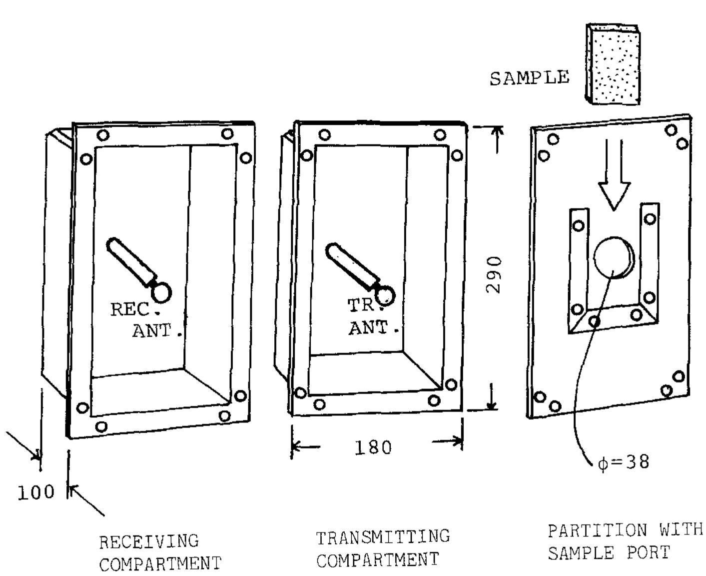


Figure 2 The shielding box.

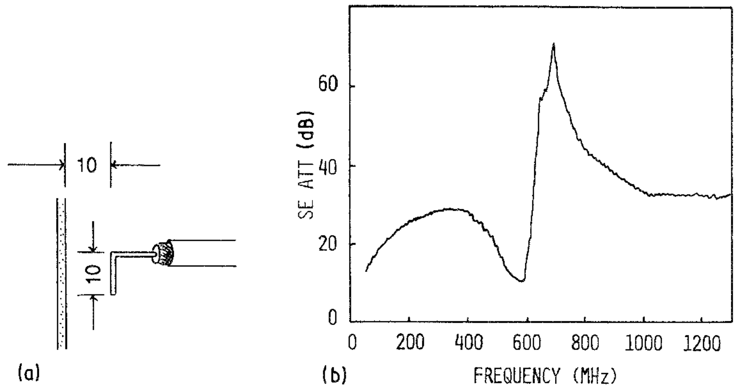


Figure 3 (a) Small dipole antenna, (b) transmission characteristics of the measuring equipment with antenna (a) without the sample.

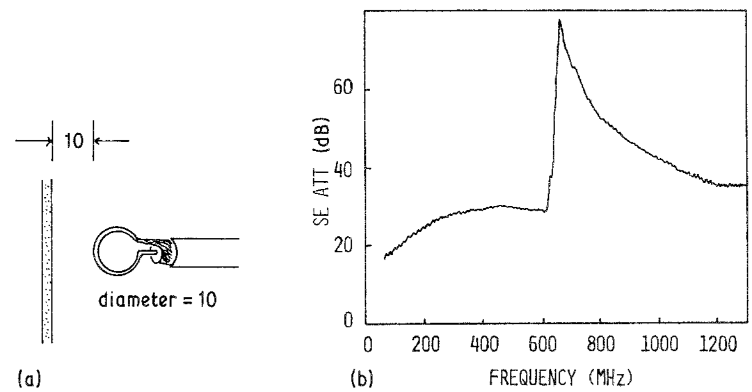


Figure 4 (a) Small loop antenna, (b) transmission characteristics of the measuring equipment with antenna (a) without the sample.

9S (Ajinomoto Co. Ltd):

$$CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}OTi(O\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}{-}C_6H_4C_{12}H_{25})_3$$

Aluminium fillers (54 g) were dispersed in 300 ml acetone (for esters) or hexane (for coupling agents) containing 0.2 ml of the reagents for 30 min, and the solvent was removed under reduced pressure.

3. Results and discussion

3.1. Effect of filler concentration

It is well known that the aspect ratio of fillers is important for the generation of the electrical conductivity of the composites and fibrous fillers, especially chatter-machined short-length metal fibres which are superior to other conductive fillers such as powdery particles or flakes [15]. To confirm the superiority of the chatter-machined metal fibres, initially a series of composites containing different amounts of filler were prepared using four kinds of aluminium fillers, namely, flake, shaved flake, melt-spun short-length fibre and chatter-machined short-length fibre.

As shown in Fig. 5, the electrical conductivity of the composites prepared with fibrous fillers is higher than that of the flakes, and especially so in the chatter-machined aluminium fibre which gives the best composite among the fillers examined.

A series of composites were successively prepared using various chatter-machined metal fibres and carbon fibre, and the relationship between specific resistance and concentration of fillers were examined. As shown in Fig. 6 the electrical conductivity of the composites prepared is obviously dependent on the kind of the fillers and the order of the effectiveness is brass > steel > copper ≈ aluminium > carbon. The order does not necessarily correspond to that of the pure fillers (see Table I).

According to Katayama [3, 16, 17], specific resistance of the composites can be the summation of specific resistance of pure fillers and contact resistance between the fillers. The presence of an oxidized surface

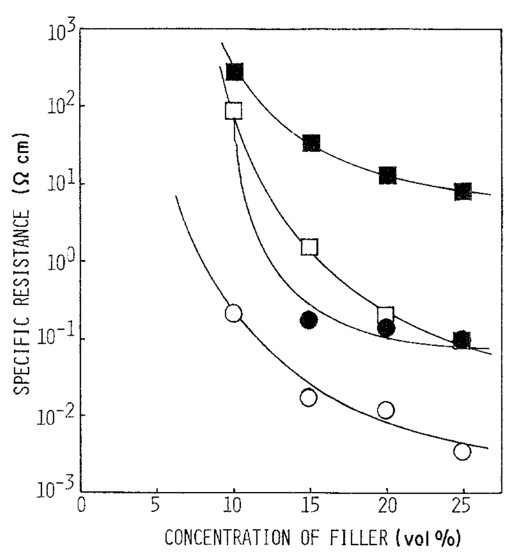


Figure 5 A plot of specific resistance against aluminium filler concentration in PE series composites. (○) Chatter-machined fibre, (●) melt-spun fibre, (□) shaved flake, (■) flake.

TABLE I Specific resistance and specific gravity of fillers

Filler	Specific resistance (Ωcm)	Specific gravity ($g\,cm^{-3}$)
Aluminium	2.7×10^{-6}	2.7
Copper	1.7×10^{-6}	8.9
Iron	9.8×10^{-6}	7.9
Brass	6 to 7×10^{-6}	8.4
Carbon fibre	10^{-3} to 10^{-1}	1.7

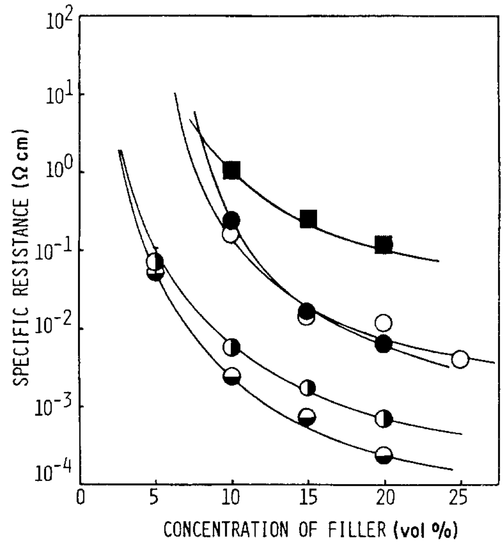


Figure 6 A plot of specific resistance against concentration of short-length metal fibres and carbon fibre in PE series composites. (○) Al, (◒) brass, (●) Cu, (■) carbon fibre, (◑) Fe.

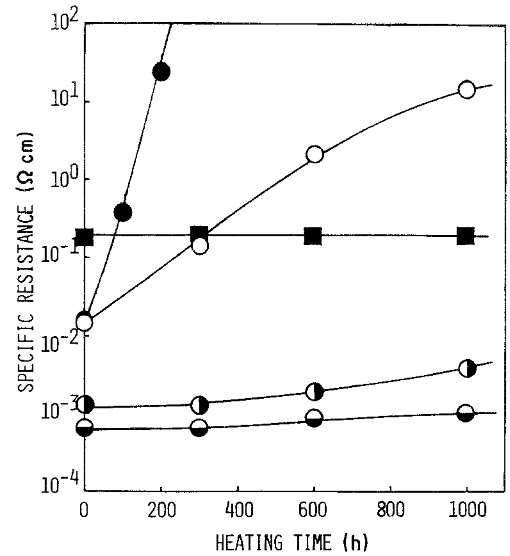


Figure 8 Changes in specific resistance of metal fibres (15 vol %)– or carbon fibre (20 vol %)–, PE composites during heating in air at 80° C. (○) Al, (◒) brass, (●) Cu, (■) carbon fibre, (◑) Fe.

covered with an adsorbed layer in the surface region of metals is also well known [18–20]. Therefore, the contact resistance between the fillers which relates to the oxidized surface of the fillers plays a very important role for the electrical conductivity of the composites.

Shielding effectiveness of electromagnetic interference of the composites was also examined and the results obtained are shown in Fig. 7 where shielding effectiveness of electric and magnetic field modes at 250 and 1200 MHz are compared, separately.

From Fig. 7 it is obvious that the shielding effectiveness is dependent on the kind of electromagnetic waves and their wave length. Namely, shielding of the electric field in the low-frequency wave region (250 MHz) is easy, but not in the higher region (1200 MHz). While shielding of the magnetic field is very difficult at lower filler concentrations in both low- and high-frequency wave regions. However, in general the shielding effectiveness of electromagnetic interference of the composites is fairly consistent with the electrical conductivity mentioned above. From the results, successive experiments were carried out using composites containing 15 vol % chatter-machined short-length metal fibres and 20 vol % short-length carbon fibre.

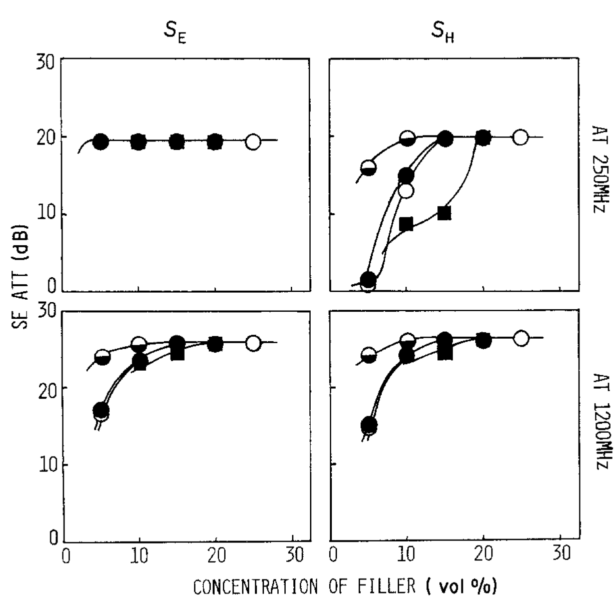


Figure 7 A plot of shielding effectiveness against concentration of short-length metal fibres and carbon fibre in PE series composites. (○) Al, (◒) brass, (●) Cu, (■) carbon fibre. S_E, electric field; S_H, magnetic field.

3.2. Thermal stability of shielding effectiveness

A series of composites containing 15 vol % chatter-machined metal fibres and 20 vol % carbon fibre were heated in an electric oven at 80° C in air for various times, and the thermal stabilities of the electrical conductivity and the shielding effectiveness were examined.

As shown in Fig. 8, during the thermal treatment, changes in the specific resistance were scarcely observed in the carbon fibre system and fairly slight increases in the specific resistance were observed in brass and steel systems after 1000 h. However, remarkable increases in the specific resistance were observed in copper and aluminium systems, especially in the former.

Similar results were observed for the shielding effectiveness of electromagnetic interference of the composites examined (see Fig. 9).

To elucidate the reason for the thermal degradation of the shielding effectiveness of the copper and aluminium composite systems, thermal treatment was carried out in a vacuum oven at 80° C. As shown in Fig. 10, increase in the specific resistance of both the composites is much slower in a vacuum than that in air which implies that oxygen or moisture plays a very important role for the degradation of the shielding effectiveness of the composites.

To examine the effect of preheating of the fillers or oxidized surface on the electrical conductivity, composites were prepared using both copper and aluminium fillers which had been pretreated at 80° C in air. As shown in Fig. 11, preheating of the metal fillers does not affect the specific resistance values of the composites not subjected to thermal treatment. The

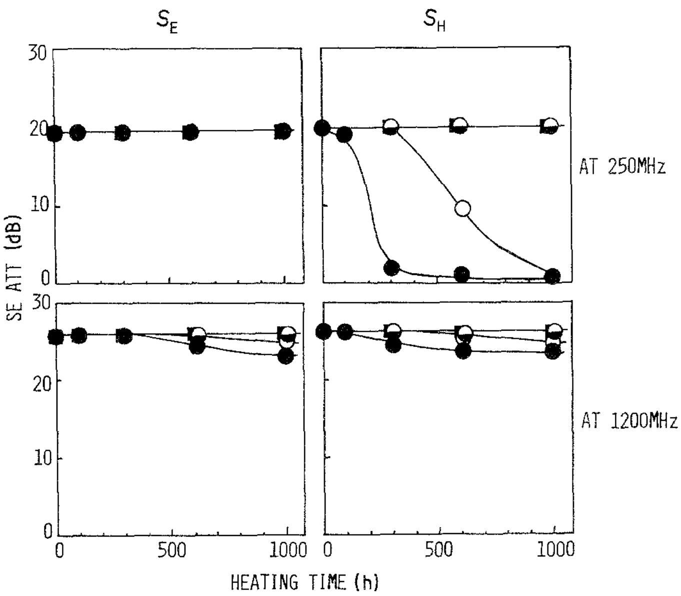


Figure 9 Changes in shielding effectiveness of metal fibres (15 vol %)– or carbon fibre (20 vol %)–PE composites during heating in air at 80° C. (○) Al, (◒) brass, (●) Cu, (■) carbon fibre. S_E, electric field; S_H, magnetic field.

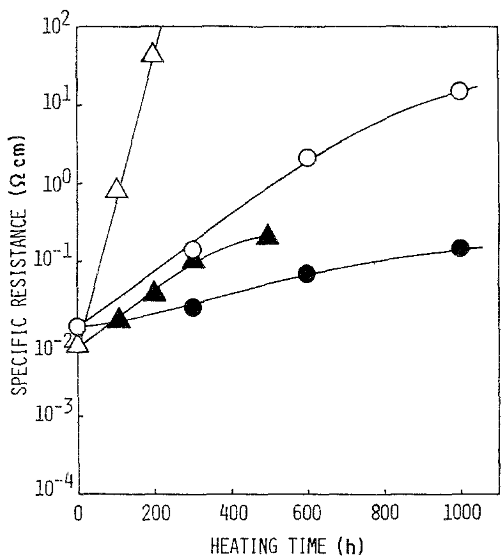


Figure 10 Changes in specific resistance of copper and aluminium fibres (15 vol %)–PE composites during heating (△, ○) in air and (▲, ●) *in vacuo* at 80° C. (△, ▲) Cu, (○, ●) Al.

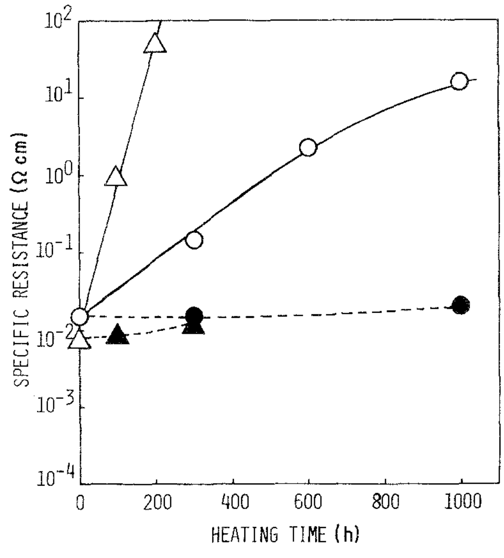


Figure 11 Changes in specific resistance of copper and aluminium fibre (15 vol %)–PE composites during heating in air at 80° C (△, Cu; ○, Al) and specific resistance of copper and aluminium fibres (15 vol %)–PE composites (without heating) whose fibres were pre-heated in air at 80° C (▲, Cu; ●, Al).

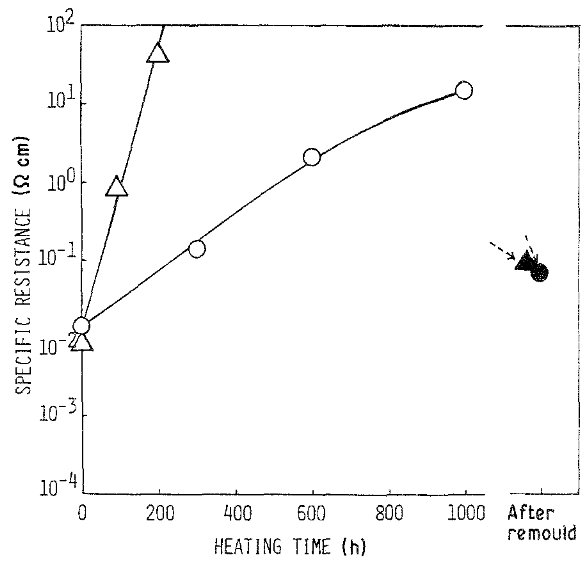


Figure 12 Changes in specific resistance of copper and aluminium fibre (15 vol %)–PE composites during heating in air at 80° C, and specific resistance of remoulded composites after heating (Cu, 300 h; Al, 1000 h).

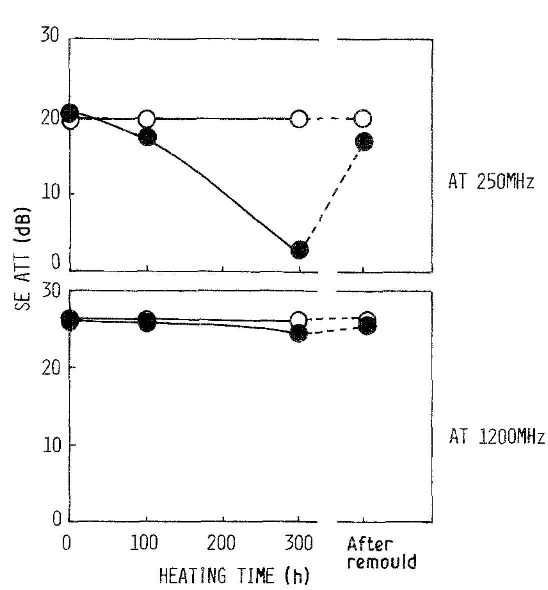


Figure 13 Changes in shielding effectiveness of copper fibre (15 vol %)–PE composite during heating in air at 80° C, shielding effectiveness of remoulded composite after heating for 300 h. (○) Electric field, (●) magnetic field.

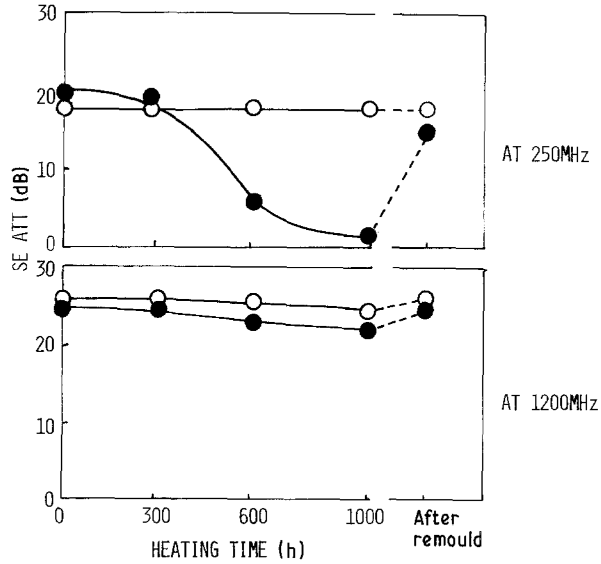


Figure 14 Changes in shielding effectiveness of aluminium fibre (15 vol %)–PE composite during heating in air at 80° C, shielding effectiveness of remoulded composite after heating for 1000 h. (○) Electric field, (●) magnetic field.

fact apparently implies that the oxidized copper or aluminium surface in the composites was removed during the preparation of the sample under high pressure.

If the assumption is true, the shielding effectiveness of the thermally degraded composites should be recovered by remoulding under mechanical stress such as pressure. Accordingly, thermally treated composites (1000 h for the aluminium system and 300 h for the copper system) were crushed by a hammer under chilled conditions and remoulded; then the shielding effectiveness of these remoulded composites was examined. As shown in Fig. 12, the specific resistance

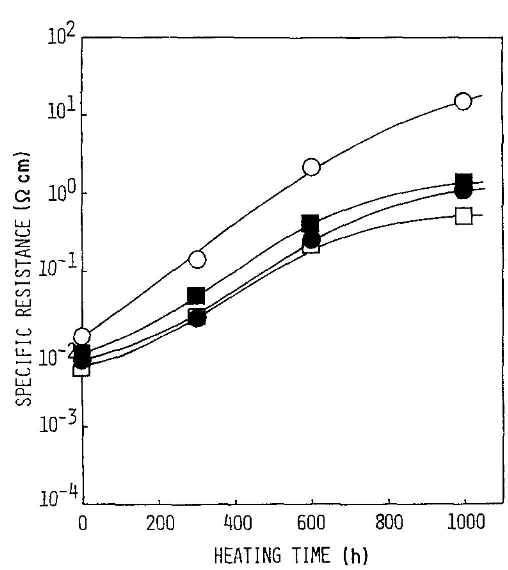
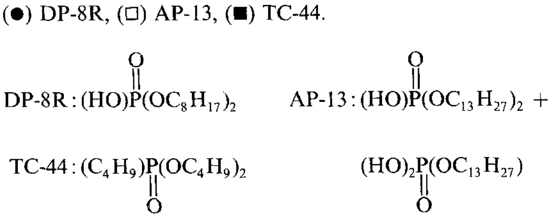


Figure 15 Changes in specific resistance of aluminium fibre (15 vol %)–PE, and aluminium fibre (15 vol %) pretreated with phosphates–PE composites during heating in air at 80° C. (○) Al only, (●) DP-8R, (□) AP-13, (■) TC-44.



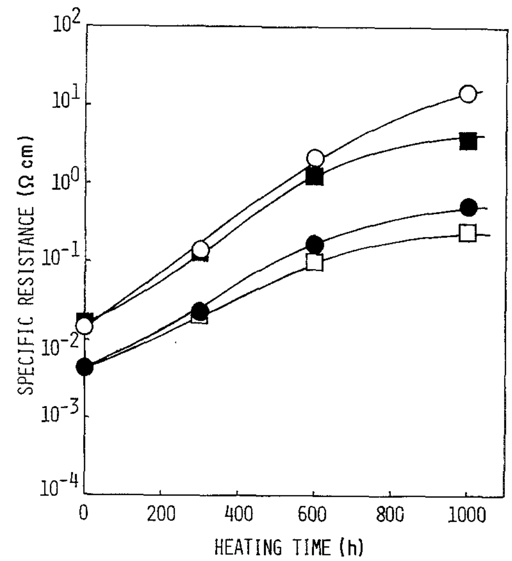
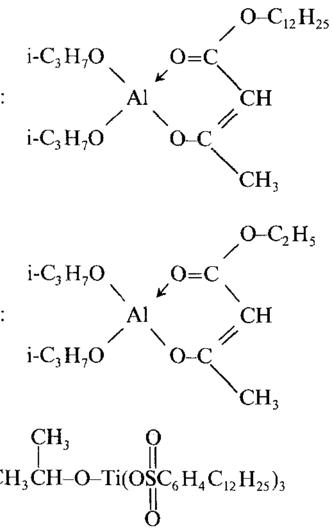


Figure 16 Changes in specific resistance of aluminium fibre (15 vol %)–PE, and aluminium fibre (15 vol %) pretreated with coupling agents–PE composites during heating in air at 80° C. (○) Al only, (●) AL-M, (□) 9S, (■) ALTC.



of the remoulded composites decreases somewhat, and the electrical conductivity recovers appreciably again. The results definitely support the assumption mentioned above.

In this context, the role of the thermal oxidative degradation of polyethylene matrix should be taken into account. However, infrared spectra of the polyethylene extracted from the thermally degraded composites which had been crushed into small pieces under chilled conditions showed no evidence of the formation of oxygenated functional groups in the carbonyl region (1720 cm^{-1}).

In addition to the electrical conductivity of the composites, we also examined the effects of thermal treatment and remoulding of the copper and aluminium composites on the shielding effectiveness of electromagnetic interference. As shown in Figs 13 and 14, the shielding effectiveness of the composites decreases during the thermal treatment but recovers remarkably on remoulding the degraded samples.

The results obtained from the series of experiments suggest that the original oxidized surface of the copper or aluminium fibre was removed during preparation of the composites under pressure, but new oxidized surface is formed in the composites by the thermal treatment. The newly formed oxidized surface also increases the contact resistance between the metal fillers to reduce the shielding effectiveness of electromagnetic interference of the composites.

3.3. Inhibition of the degradation of shielding effectiveness

Among the chatter-machined fibrous metal fillers examined, aluminium fibre is the most suitable one from the economical and weight (see Table I, s.g. 2.7) points of view, but the degradation of the shielding effectiveness of the composite during use at elevated temperatures apparently restricts commercial production. Therefore, inhibition of the thermal degradation of the shielding effectiveness was attempted for the aluminium composite system.

A series of aluminium composites was prepared using the chatter-machined short fibres previously treated with various phosphates and coupling agents, and changes in the specific resistance during thermal treatment was examined. As shown in Figs 15 and 16, the thermal degradation of electrical conductivity of the aluminium composite could be retarded to some extent by the treatment of the aluminium fibre surface with some reagents. The stabilization of the aluminium composite for practical use is under investigation.

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