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EFFECTS OF CRYOGENIC TREATMENT ON THE PROPERTIES OF TYRE PRODUCTION WASTES

BAĞDAGÜL KARAAĞAÇ*[a], **VELİ DENİZ**[a],
and MURAT ŞEN[b]

[a] *Kocaeli University, Engineering Faculty, Chemical Engineering Dept, Umuttepe Campus, 41380 Kocaeli / Turkey*
[b] *Hacettepe University, Faculty of Science, Chemistry Dept. Beytepe Campus, 06800 Ankara / Turkey*
bkaraagac@kocaeli.edu.tr, vdeniz@kocaeli.edu.tr, msen@hacettepe.edu.tr

Abstract

It has not been reported any methodology in literature for recycling of calendared metallic fabric and green tyre wastes produced in tyre industry. They are either recycled after vulcanization or disposed by environmentally unfriendly methods. In this study, the conditions of cryogenic recycling of metallic fabric wastes from tyre manufacturing process and the possibility of reuse compound part on these wastes have been investigated. Solid CO_2 and liquid N_2 were used as coolants. Cold and brittle material was separated into two phases as rubber compound and steel by mechanical treatment. The changes in rheological, physical and mechanical properties of the compounds after recycling were studied. Adhesion strength, rheological and mechanical properties of compounds that obtained from the wastes were deteriorated by a maximum of 10 % with decreasing dispersion quality. It has been concluded that cryogenic technique can be used for recycling of reinforcing materials such as calendared metallic fabric and green tyre wastes in tyre industry without significant decrease in their commercial values.

Introduction

In recent years, production rate of rubber industry and polymeric material consumption have been increased in parallel to rapid industrialization and civilization. Since the polymeric materials do not decompose easily, disposal of waste polymers is a major environmental problem for both municipalities and governments. A variety of global and national policies are being developed and proposed worldwide related to disposal of solid wastes such as plastics and waste rubber tyres.

Tyre components are mainly elastomers (synthetic and/or natural rubber), fillers, polymeric and metallic cords and chemical additives. The proportion of the components depends on type or specific use of tyre. If tyre scraps are land filled in incorrect way, they may be inevitably leached out into the surrounding environment and cause soil and marine pollution, directly. And they may cause air pollution because of possible fire emissions, PAHs and ash. Since most of these wastes contain petroleum based products, re-use and/or recycling of those wastes are also very important to keep unrenewable resources. But, raw materials in used tyres are not directly reusable, because of the network structure of vulcanized rubber. For these reasons, it needs a devulcanization process or a suitable degradation process for regeneration or recovery of its materials. There are some significant attempts for material recycling and energy recovery from tyre wastes. However, a considerable part of used tyres and the other tyre based wastes are being disposed by using conventional environmentally unfriendly techniques, over the world. Land filling of used tyres is still widely in use in many countries. In EU, according to EC directive 1999/31/EC, land filling of whole tyres and shredded tyres was banned as of 16th July of 2003 and 16th July of 2006, respectively. In Turkey, for the aim of adaptation to EU regulations, legislative operations have just been put into practice as of the 1st January of 2007. According to this regulation, waste tyres are described as hazardous wastes and import activities were banned. The people and/or facilities who cause environmental pollution about waste tyres have to pay the expenses to compensate consisting harms.

Wastes of tyre industry can be classified as used tyres, retreading process wastes, laboratory scraps, inner tube and bladder wastes, green tyre wastes, reinforcing material wastes and other compound scraps. Among these, major part is used tyres that are almost $14x10^6$ tonnes/year, which is approximately 2 % of total solid waste production in the world. $4.5x10^6$ tonnes are produced in USA and $3.2x10^6$ tonnes in Europe. In Turkey, this amount has been estimated as 250 000 tonnes/year[1].

Recent waste management strategies focus on prevention of wastes. Therefore, any kind of wastes should be reduced as much as possible where they are produced. In recycling plants, each kind of vulcanized and unvulcanized wastes can be recycled by various techniques[2]. In reinforcing materials group, textile fabric wastes can be recycled as regenerated rubber after removing the textile component[3]. It is difficult to separate the rubber compound and metallic cord in the calendared fabric and/or green tyres due to its sticky character. In many applications, these wastes are vulcanized in an autoclave and then recycled with the other vulcanized wastes. Beside this, metallic fabric wastes are frequently burned in the field only for recovering metallic cord. This is an illegal and environmentally unfriendly disposal way. There is not any methodology for recycling raw material of green tyres and metallic fabric wastes in literature.

In the case of a tyre is not deteriorated during its first life, it can be retread and reused again. This is the most effective way to reduce tyre based wastes. When the tread wear index (depth of tread notches) of an automobile tyre is equal or smaller than 1.6, that means that tyre is not appropriate to run anymore because of abrasion, we can strip the tread part and re-mould the tyre with a new tread. However, if the conditions are not appropriate for retreading, some other recycling techniques should be considered. Material recycling methods can be simply classified as mechanical and cryogenic grinding, microwave, ultrasonic and chemical recycling techniques. Pyrolysis can be counted in this group. Mechanical grinding is the easiest recycling process. Tyres are shredded and then ground into small particles. In microwave and ultrasonic techniques, indirect energy sources are used to cleave C-S and S-S bonds in vulcanized waste material without depolymerization of the main chain. There is an important restriction in microwave technique; waste material must be polar in order that microwave energy will generate required heat for devulcanization. In chemical recycling methods, ground and refined waste material is substantially devulcanized using some devulcanization agents. Most common devulcanization agents are dibenzyl disulphur, diphenil disulphur, diamyl disulphur, phenolic disulphurs, bis (alchoxy aryl) disulphurs, butyl mercaptans, xylene mercaptans, butyl tiophenols and xylene tiols. In pyrolysis process, waste material is degraded with heating in an oxygen-free atmosphere to get carbon black, oil and fuel gas[4].

Tyre industry's wastes consist significant amount of organic substances. They have comparable calorific values and relatively low hazardous emissions with other solid and liquid fuels[5]. Thus, used tyres are widely used in cement kilns as an alternative or secondary fuel[6].

Cryogenic grinding of various parts of vulcanized wastes is an old and widely used recycling technique[7]. Liquid N_2 is the most preferred cryogenic medium. Application of solid CO_2 that could be met in literature is very limited. Solid CO_2 has been used for assisting ball milling and generating post-consumer polymeric materials[8]. Smaller rubber particles can be obtained in this method. Cryogenic mechanical alloying was also investigated to produce highly dispersed blends composed of thermoplastics and tyre, thereby providing a potentially new route by which to recycle discarded tyres[9].

In this study, the conditions of cryogenic recycling of metallic fabric wastes and the possibility of reusing the compounds separated from wastes have been investigated.

Experimental

Material

Metallic fabric wastes used in this study were obtained from local tyre manufacturing plants in Kocaeli, Turkey. And some of them are from automobile, some are from truck tyre those represent the different compound composition.

Method

Glass transition temperatures (T_g) of different compounds which were mechanically separated from metallic fabric wastes have been firstly determined using differential scanning calorimetry. The temperature in the waste bulk during cryogenic treatment is measured by Tastotherm MP 2000 model thermometer with an iron-constantan thermocouple. Solid CO_2 and liquid N_2 were used as coolants. Cold and brittle material was separated into two phases as rubber compound and steel by mechanical treatment. Rubber compounds were mixed on a two-roll mill for 5 minutes and sheets were prepared for further tests. Mooney viscosities of the compounds were measured by a Mooney viscometer (Alpha MV2000) according to ISO 289-1. Rheological properties were determined using a moving die rheometer (Alpha MDR2000) according to ISO 3417. Compounds were vulcanized under a pressure of 13.7 MPa in for specified cure time at 170 ºC. Hardness values of the samples were measured using a durometer according to ASTM D2240 and mechanical properties were measured using a tensometer (Monsanto T10) according to ASTM D412. Dispergrader 1000 NT was used for measuring dispersion quality of the compounds. Adhesion strength was measured using Pirelli peeling test method.

Results and discussion

T_g value is critical for cryogenic recycling, because it effects the processing temperatures. Therefore, T_g values of different skim compounds separated from metallic fabric wastes have been firstly determined. It was found that these values were in a range of -40 and -60 ºC as shown in Table I. These results show that skim compounds show similar cooling characteristics and each wastes even they are from different sources can be recycled within a narrow temperature range.

Table I
Tg values of the compounds studied

Sample No	Tg [ºC]
1	–47.1
2	–47.1
3	–46.6
4	–50.3
5	–44.9
6	–42.1
7	–44.9
8	–50.4
9	–51.8
10	–50.2
11	–50.1
12	–48.9

Cooling time of the wastes depend on the type of coolant and thickness of the waste, strictly. Because, waste bulk thickness is directly affect heat transfer rate and so time and price of the operation. With a preliminary analysis, cooling times of wastes which have various thicknesses to feed into the experimental setup are shown in Figure 1.a and 1.b. It is shown that the cooling time in both type of coolants depends on the amount of waste only. As expected, wastes cool faster in liquid N_2.

Average changes in the compound properties after cryogenic and mechanical treatment of the wastes, are shown in Fig. 2. It was concluded that remixing the skim compound caused a decrease in Money viscosity. Scorch time, tensile strength and elongation at break were deteriorated as maximum 10 % by cryogenic and mechanical treatment in both coolants. On the other hand, 300 % modulus was increased and only a little change in hardness was observed. Cryogenic and mechanical treatment also decreased adhesion strength of

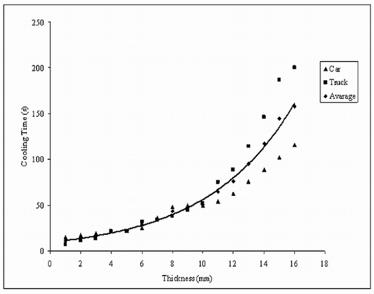

Fig. 1.b. **Cooling times in solid N_2 for increased sample thicknesses**

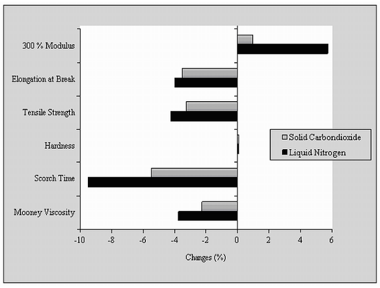

Fig. 2. **Average changes in compound properties by cryogenic and nechanical treatment**

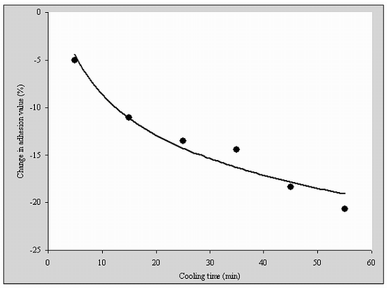

Fig. 3. **The changes in adhesion strength of the compounds**

the compounds. This can be seen in Fig. 3 for various exposure time.

Significant decrease in adhesion strength is attributed to decrease in dispersion quality of the compounds. As these compounds were in glassy state below their T_g's, chemical additives in the compounds would be migrated towards to outer surfaces depending on their melting points and the molecular weights during repetitive cooling and reheating stages. Poor dispersion quality may also cause a decrease in mechanical properties.

To verify these changes in compound properties, the dispersion quality of recycled compound samples was studied and compared with the untreated sample using a dispergrader. In this method, number of small agglomerates is a measure of dispersion quality. The results of dispersion measurement are shown in Fig. 4. The initial dispersion quality of the untreated compound is represented as certain level of the agglomerate size depending of their mixing history. As the cooling time increases the number of small agglomerates decreased sharply. It can be concluded that cryogenic and mechanical treatment decreases dispersion quality of the compound, resulting with a slight deterioration of some mechanical properties.

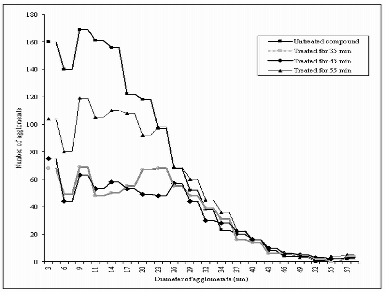

Fig. 4. **Changes in number of agglomerates by cryogenic and mechanical treatment**

Conclusions

In this study, the conditions of cryogenic recycling of metallic fabric wastes produced in tyre industry were investigated. It has been observed that -60 ºC is optimal for a reasonable operation condition. The cooling of wastes by using solid CO_2 seems to be possible. However, considering many difficulties for spraying solid CO_2 during the operation, it was concluded that solid CO_2 is not a suitable coolant for this purpose. Adhesion strength, rheological and mechanical properties of compounds obtained from the wastes are deteriorated by a maximum of 10 % with decreasing dispersion quality. In conclusion, cryogenic technique can be used for recycling of reinforcing materials such as calendared metallic fabric and green tyre wastes of tyre industry without remarkable decrease in their commercial values.

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POLYMER-BASED COMPOSITES FOR MINIMIZATION OF EMI IN AUTOMOBILE ELECTRONIC SYSTEMS

RASTISLAV DOSOUDIL*, MARIANNA UŠÁKOVÁ, and JOZEF SLÁMA

Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Department of Electromagnetic Theory, Ilkovičova 3, 812 19 Bratislava, Slovakia
rastislav.dosoudil@stuba.sk

Abstract

FeSi/PVC composite materials with different filler concentrations (10, 20, 30, 40, 50 and 60 vol.%) were prepared using a dry low-temperature hot-pressing process (at 135 °C and 5 MPa) and the electromagnetic wave (EM-wave) absorption properties have been investigated by means of a coaxial S-parameter method in the frequency range from 1 to 3000 MHz. The return loss (RL), matching frequency (f_m), matching thickness (d_m), and the bandwidth (λf) for $RL \leq -20$ dB were numerically simulated by a simple program. Decreasing the FeSi content in the composite, the matching frequency increases, the matching thickness decreases and the bandwidth enlarges. Compared with spinel ferrite/polymer absorbers, the absorbers with conductive magnetic filler have better absorbing properties, such as a thinner matching thickness and a wider EM-wave bandwidth.

Introduction

The rapid evolution of high-speed digital electronics, wireless communication and/or navigate systems, and control electronic equipments used in automobiles necessitates the development of effective, compact, and economical absorbers of electromagnetic energy to ensure electromagnetic compatibility and ecological safety in a wide frequency range. Since polymer-based composite materials have the advantage of easy processing, low density, flexibility and tuneable properties, they have attracted much attention for the applications to the electromagnetic wave (EM-wave) absorber, electromagnetic interference (EMI) noise suppressor and inductor. Ferrite, iron-based powders, dielectrics and conductive materials are generally filled in the polymer matrices to render the polymer composites the effective electromagnetic properties. Magnetic fillers such as soft ferrites (possessing a unique combination of high permeability and extremely low dc electrical conductivity) are frequently used in composites to make wideband absorbers. Frequency dispersion of complex permeability of such composites can be controlled by variation of the composite filler concentration, size of inclusions, and their morphology. Attempts are also made to control the magnetic properties of inclusions through the microstructure of composites, etc. However, the permeability and the maximum loss frequency (resonance frequency) are related according to Snoek's law, limiting the bandwidth for spinel ferrite-based composites' applications as microwave absorbers[1,2]. One of the possibilities is to use a conductive soft magnetic material as filler in composite because its permeability at high frequencies is not limited by Snoek's low.

In this study, we have developed the FeSi/PVC composite materials with various soft magnetic FeSi powder filler concentrations 10-60 vol.% to investigate the electromagnetic absorbing properties in the frequency range from 1 to 3000 MHz using vector network analysis method.

Experimental

We used a commercially available FeSi alloy random-shaped particles (Kovohuty, Dolný Kubín, Slovakia) with less than 100 μm diameter. The shape and size of particles were confirmed by Scanning electron microscopy (SEM), Fig. 1.

The chemical composition of FeSi powder is summarized in Table I. This powder was mixed with polyvinylchloride (PVC) to make metal alloy/polymer composite materials. The filler concentration varied as follows: 10, 20, 30, 40, 50 and 60 vol.%. The composites were prepared by means of a dry low-temperature hot-pressing process (at a temperature of 135 °C and a pressure of about 5 MPa).

The composite specimens for measuring the permeability were precisely machined to become the coaxial (toroidal) shape with the inner and outer diameter of 3.1 and 7 mm, respectively, and the thickness of 1.9-2.5 mm. The complex (relative) permeability $\mu = \mu' - j\mu''$ was measured in the frequency range from 1 to 3000 MHz by using two vector network analyzers (HP 4191A and Agilent 8714ET) and a coaxial holder (Agilent 16454A). The S-parameter method was adopted for obtaining the complex permeability. Calibration was conducted with open/short/load standards prior to measurements[3].

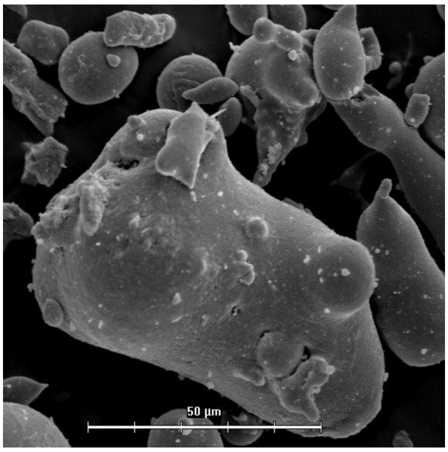

Fig. 1. **SEM photograph of FeSi powder filler**

Table I
Chemical composition of FeSi particles

Element	Fe	Si	C	Al	Mn	Cr
Content [%]	82.5	15.0	0.8	0.3	1.0	0.4

Results and discussions

Frequency dependences of complex permeability $\mu = \mu' - j\mu''$ are plotted in Fig. 2 for prepared composite materials; the parameter of plots is filler concentration. The resonance frequency of composites, f_r, at which the imaginary part μ'' of permeability μ has a maximum value, is shown in Table II. The real part μ' of permeability μ monotonically decreased and the difference in the values due to the filler concentration is reduced with increasing frequency, while the imaginary μ'' values are slightly increased with increasing frequency at first, then reached a maximum value (at f_r) followed by a moderate decrease; the difference in the value at a given frequency seems to be increased with the filler concentration. The μ''-f curves (f is the frequency of applied ac electromagnetic field) in Fig. 2 also indicate that the high value of real permeability μ' should be required in order to have the high value of imaginary permeability μ'' (the high value of μ'' is important for EM-wave absorber design).

The achieved type of permeability dispersion can be explained as follows. The magnetic materials possess two basic magnetizing mechanisms that can affect the permeability dispersion, namely the domain wall displacement and the spin precession. The former is obviously present in multi-domain magnetic particles and in the frequency region up to about 50 MHz (over this frequency the domain wall cannot keep the pace with high frequency ac applied field and starts to remain behind), so that the contribution of domain wall resonance is probably negligibly small. The latter is the cause of spin precession (or natural ferromagnetic) resonance and is present mainly in GHz range. In case of conductive magnetic materials (such as FeSi alloy filler in the produced composites) also the presence of eddy currents influenced the measured permeability spectra. Therefore the permeability values (both real μ' and imaginary μ^2) are high enough in GHz frequency range to develop thin and flexible EM-wave absorbers for EMI reduction in automobile electronic systems.

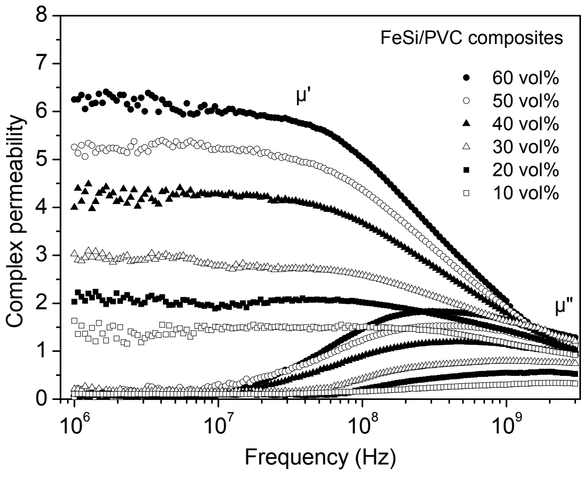

Fig. 2. **Complex permeability as a function of frequency for FeSi/PVC composites**

Table II
Resonance frequency, f_r, of FeSi/PVC composites

Filler content [vol.%]	60	50	40	30	20	10
f_r [MHz]	289	347	405	973	1311	1964

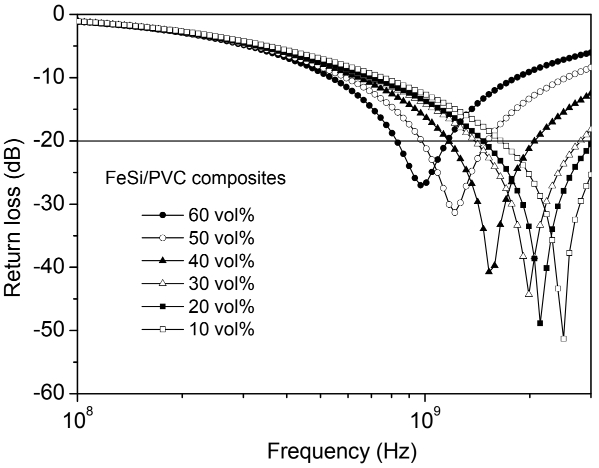

Fig. 3. **Return loss as a function of frequency for FeSi/PVC composites**

Numerical simulation for return loss, RL, of single-layer metal-backed absorber was carried out using the following equation[2,4]:

$$\mathrm{RL} = 20\log\left|\frac{j\mu\dfrac{2\pi}{\lambda}d-1}{j\mu\dfrac{2\pi}{\lambda}d+1}\right| \tag{1}$$

where ℓ is the wavelength of applied ac electromagnetic field and d is the thickness of the absorber. The equation was derived under assumption that d is small enough compared with ℓ. The RL is minimal when $j\mu 2\pi d/\lambda = 1$ (matching condition) which allows calculating the matching thickness[5]:

$$d = d_m = \frac{\lambda}{2\pi\mu''} = \frac{c}{2\pi f_m \mu''(f_m)} \tag{2}$$

with c the speed of light, f_m the matching frequency and $\mu''(f_m)$ denotes μ'' at $f = f_m$. A composite works as a perfect absorber when the matching condition is fulfil (i.e. when the thickness of an absorber is equal to matching thickness, the frequency of applied field is equal to matching frequency and the return loss reached its minimum value).

Fig. 3 plots the variation of return loss versus frequency for produced composites. The horizontal line stands for the determination of the -20 dB bandwidth (the bandwidth Δf corresponds to the frequency interval in which the return loss is less than -20 dB). Table III lists the data of absorption properties for the prepared composites (matching frequency f_m, matching thickness d_m and the bandwidth Δf for $RL \leq -20$ dB). With decreasing the filler concentration in composites, the f_m and Δf rose while the d_m slightly decreased. Matching frequency f_m of absorbers was higher than their resonance frequency f_r. Therefore, the spin precession resonance (as the main loss mechanism) is responsible for the composite absorption properties. The eddy current loss could also contribute to the f_m enhancement. From Fig. 3 and Table III it can also be noticed that by decreasing the FeSi content in the composite, the absorption in the sample can be increased and it also reduces the absorber thickness.

Table III
Absorption parameters of FeSi/PVC composites

Filler content [vol.%]	60	50	40	30	20	10
f_m [MHz]	965	1304	1550	2012	2180	2340
d_m [mm]	5.7	5.4	5.0	4.7	4.4	4.0
Δf [MHz]	496	530	907	1403	1516	>2000

The dip showing minimum RL as observed in Fig. 3 shifts towards a higher frequency side. This behaviour can be understood based on quarter-wave principle. When an electromagnetic wave is incident on an absorber sample backed by a metal plate, it is partially reflected from air to absorber interface and partially reflected from absorber to metal interface. These two reflected waves are out-of-phase by 180° and cancel each other at air/absorber interface for the absorber satisfying the quarter-wave thickness criterion[2]:

$$d_m \approx \frac{1}{4 f_m \sqrt{\mu'} \left(1 + \tan^2 \dfrac{\mu''}{\mu'} \right)} \qquad (3)$$

Since the d_m is inversely proportional to f_m, the above criterion is satisfied at reduced sample thickness for higher frequencies. The higher absorption at reduced thickness is the result of total cancelation, satisfying the above criterion perfectly.

Summary

Soft magnetic composites with FeSi alloy filler and dielectric PVC polymer matrix were prepared to study the frequency dispersion of magnetic permeability and EM-wave absorbing properties in the frequency range 1-3000 MHz. The permeability dispersion was influenced mainly by spin precession resonance and eddy current effect. We have designed EM-wave absorbers using these composite materials, which are thin, flexible and have broad absorption characteristics. Thus, the prepared FeSi/PVC absorbers can be utilized in electronic communication and control systems used in automobiles to minimize the EMI effect.

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