

Effect of Titanate Coupling Agent on Electromagnetic Interference Shielding Effectiveness and Mechanical Properties of PC-ABS-NCF Composite

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SYNOPSIS

Nickel-coated carbon fibers (NCF) treated with a coupling agent (CA) have been used for preparing composites of polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) (90/10%) by melt blending. These composites have been evaluated for electromagnetic interference shielding effectiveness (EMI SE), mechanical properties, dispersion, and adhesion of the polymer to a filler using the scanning electron microscope (SEM). There is an improvement in the EMI SE, tensile strength, and impact strength of the composite when the carbon fiber is coupled with titanate CA. In loading NCF in composite, the optimum concentration of the CA Lica 38 used is about 2.0 phf combined with 1.5 phf calcium stearate (Ca.st.) (on the weight percentage of fillers); the composite can reach an SE of 50 dB by the coaxial transmission line test method.

INTRODUCTION

The housing of electronic appliances is mostly in plastics now. In line with the expanding applications, however, there has arisen a serious problem as a result of the electromagnetic interference (EMI), formerly known as radio frequency interference (RFI). It is a problem caused by high-frequency electromagnetic wave generated by the electronic parts. It may create noise problems and bring about malfunction of other parts.^{1,2}

Nickel-coated carbon fiber (NCF), which combines the high strength, low weight and processability of a carbon fiber in core with the conductivity and corrosion resistance of a plated nickel in skin, is the first true, highly conductive reinforcement for EMI or RFI shielding of plastics. Nickel's retention of good contact resistance and relatively low cost make it the ideal coating choice for conductive composite shielding applications.³

Acrylonitrile-butadiene-styrene (ABS) is widely used as thermoplastics with good physical properties. However, the overall mechanical properties of ABS

are lower than those of other engineering plastics, and the heat distortion temperature (HDT) of general grades of ABS is lower than 100°C. These deficiencies have limited its application in many fields. Blending with polycarbonate (PC) may be considered as a means of increasing the performance of ABS plastics so that it can become a more competitive engineering thermoplastic.⁴

Blends or alloys of PC with ABS polymers have been commercially available for some time. They are reported to provide a useful balance of toughness, heat resistance, and ease of processing at a lower cost than that of the high-performance engineering thermoplastic PC. In the earlier work in our laboratory, we found that PC-ABS (90/10%) composition had the highest impact strength and a useful balance of mechanical properties,⁵ so we chose the PC-ABS (90/10%) to compound with NCF. The advantage of the titanate CA has generated greater interest in mineral-filled thermoplastics, and organotitanates have been widely used as coupling agents.^{6,7} However, literature on the use of the titanate CA in NCF-filled PC-ABS (90/10%) or NCF-filled ABS composites are scanty. Here, we study the shielding techniques of conductive fiber, which is filled into plastics using the melting blending method. The advantages of the conductive fiber-

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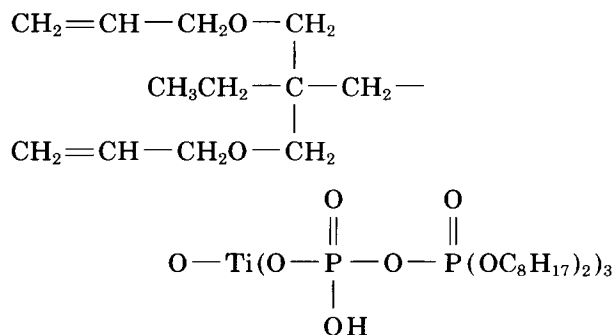
filled shielding technique are that it provides an excellent electrical conductivity, EMI SE, and steady physical properties.

EXPERIMENTAL

Materials

Acrylonitrile-butadiene-styrene (ABS), as stabilized pellets (general-purpose 5000s, trade name TAITALAC) is made by Taiwan Taita Chemical Co. Ltd. Composition: 23% acrylonitrile, 15% butadiene, 62% styrene; Melt Index (MI) = 1.5–2.5 at 200°C/5 kg. The polycarbonate used in this study was CALIBRE, a commercial product of the Dow Chemical Co., designated as general-purpose 300-22, with a melt flow rate (condition O: 300°C/1.2 kg) of 22 g/10 min. The DRY-Blend nickel-coated carbon fiber (NCF), dB910 (diameter = 7.6 μm, length = 6.5 mm) is made by American Cyanamid Co. Ltd.

The coupling agent used was neopentyl (di-allyl)oxy, tri(dioctyl)pyrophosphato titanate made by American Kenrich Petrochemicals Inc., trade name Lica 38; chemical formula:



Lubricant used was commercial-grade calcium stearate (Ca.st.). Solvents used were Liquid Chromatography (LC) grade tetrahydrofuran (THF) and EP grade isopropanol.

NCF Surface Pretreatment

The filler surface was treated with the titanate CA, Lica 38, according to the following process:

Filler + CA/solvent → stirring 3 h
 → evaporation of solvent → drying 6 h
 → pretreated filler

Compounding

Lica-38-coated fillers and ABS pellets were dried separately in a heating oven for 6 h at 80°C. The PC pellets were dried 3 h for 120°C. The samples were then blended in the Brabender Plasti-Corder Torque Rheometer, PLE-330, maintaining the following conditions: temperature 210°C, screw speed 20 rpm.

Compressing Molding

After being compounded, a batch of blended compositions could be sent into the frame and delivered into a pair of plates. When completely melted, the blend was pressed for hot compression molding at 190°C and 14.7 MPa. The ultimate pressure was kept for 4 min, and the blend was then cooled by water at a rate of 30°C/min until the temperature fell below 100°C.

Evaluation of Samples

To test the shielding effectiveness (SE) of conductive plastic composites, the coaxial transmission line method modeled on ASTM E57-83 test method was used. The sample was fixed in the center as shown in Figure 1. The SE was obtained by comparing the signals with and without the shield and measured

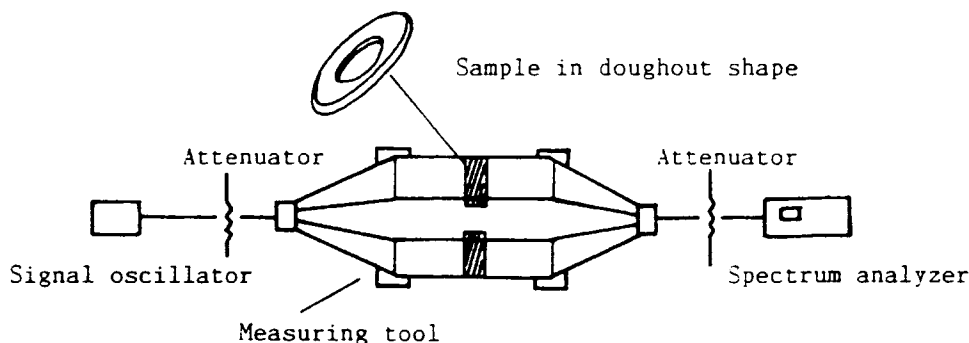


Figure 1 Construction of insertion loss measuring system (coaxial transmission circuit system).

in the range from 20 MHz to 1 GHz in which the measurement limit for this equipment was 50 dB. In order to test the surface resistivity of the material, the four-terminal method was used: In this method, four parallel wires were pressed on the sample and used as electrical contacts for surface resistivity measurements.⁸

Tensile strength was measured in accordance with ASTM D638 test method using an Instron Universal Testing Machine Model 1130. The cross-head load was 500 kg, the speed was 5 cm/min, and the chart speed was 100 cm/min.

Notched Izod impact strength was measured according to ASTM D256 test method using Izod type. The thickness of the tested samples was 0.3 ± 0.02 cm and the impact energy was at 294 J/m. The SEM showing fracture morphology of ABS filled with fillers was studied with a scanning electron microscope (Hitachi S-520).

RESULTS AND DISCUSSION

EMI Shielding Effectiveness (SE)

It is clear that the optimum CA concentration must be determined in order to obtain maximum EMI SE. The theory treats the propagation of an EM wave that passes through the walls of a shielding enclosure as a path goes through the material itself in one or more parallel paths through defects or by discontinuities in the shielding structure.^{7,9} The CA

can improve the dispersion and promote the adhesion of fibers within the material.^{7,10-14} So, the optimum CA concentration can form a network structure in which it is easier to shield the EMI wave. When greatly loaded, the fillers more easily touch each other or are close enough to allow the electrons to hop across gaps between the fibers, and the threshold percolation concentration (TPC) is reached when the infinite chain network increases. When the network structure of the fiber is formed, then the EMI wave can be better shielded than the composites, which have many discontinuity points at which the fiber aggregates. A CA not only improves the dispersion but also improves the adhesion of fillers with the matrix. By the way, the optimum CA concentration can form a network structure, which is easier to shield the EMI wave.

The EMI SE spectrums of PC-ABS (90/10%) filled with NCF are shown in Figure 2. The influence of CA concentration on the EMI SE was determined. The efficiency of the CA in improving the rheological and mechanical properties of the composite has been a subject of many publications.^{6,7} In order to arrive at the optimum concentration of this coating material for NCF, our method of EMI SE-fillers mixture was employed. The results are graphically represented in Figure 3. It can be observed that 2.0 phf CA of Lica 38 with loading 30 phr (23%) NCF used gave the best SE about 50 dB; however, a larger amount of Lica 38 failed to give any additional benefit to the characteristics of the composites.

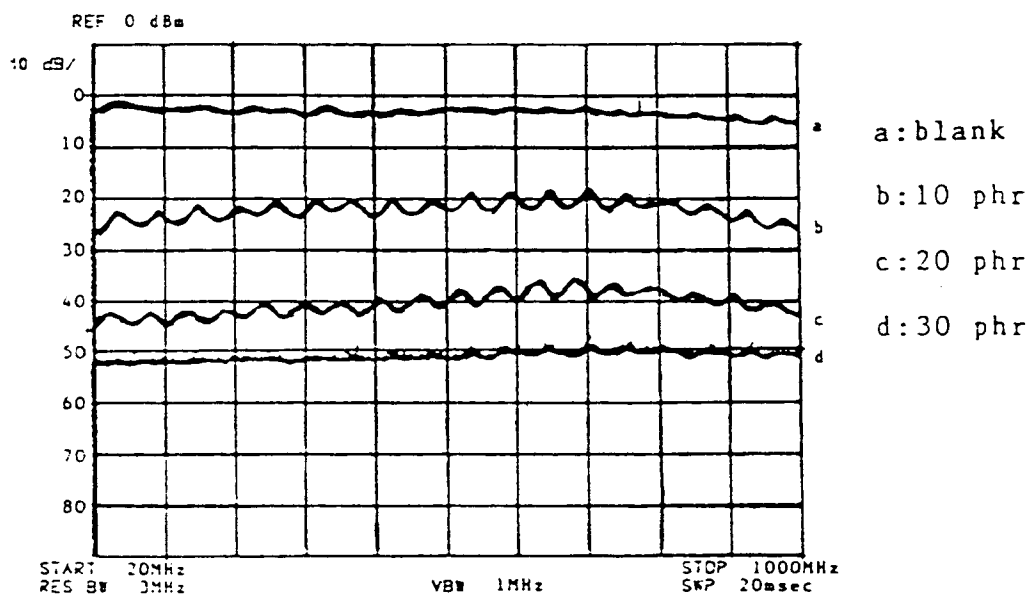


Figure 2 EMI shielding effectiveness spectrum of PC-ABS (90/10%) filled with NCF.

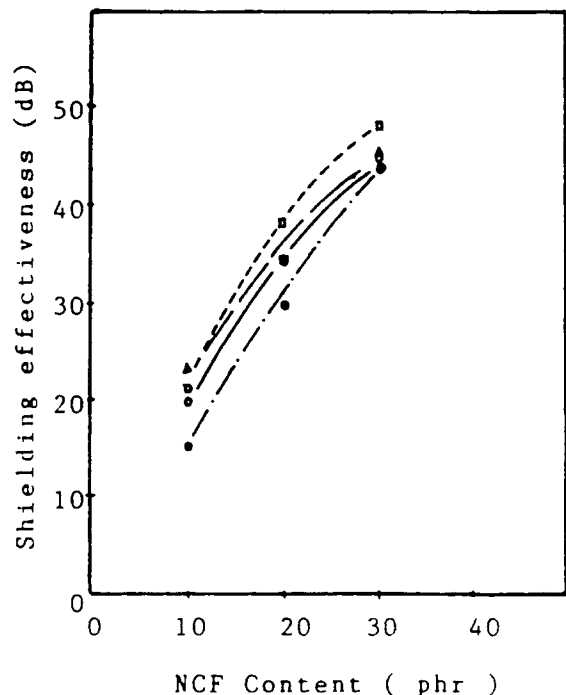


Figure 3 EMI SE of PC-ABS (90/10%) filled with NCF, coupled with (—○) 1.5 phf Ca.st., (---△) 1.5 phf Ca.st./1.5 phf Lica 38, (----□) 1.5 phf Ca.st./2.0 phf Lica 38, (—●) 1.5 phf Ca.st./2.5 phf Lica 38.

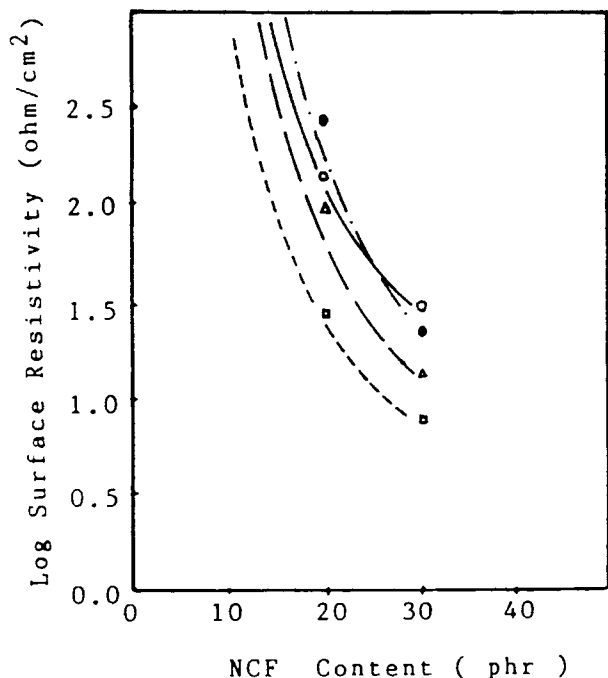


Figure 4 Surface resistivity of PC-ABS (90/10%) filled with NCF, coupled with (—○) 1.5 phf Ca.st., (---△) 1.5 phf Ca.st./1.5 phf Lica 38, (----□) 1.5 phf Ca.st./2.0 phf Lica 38, (—●) 1.5 phf Ca.st./2.5 phf Lica 38.

Surface Resistivity

This result has the same trend as resistivity decreases by several degrees at the TPC, which an effectively infinite conductive chain forms.^{15,16} Figure 4 shows that PC-ABS (90/10%)/2.0 phf Lica 38 also has the lowest value of surface resistivity. The reason is the same as the EMI shielding principle. It is apparent that a larger amount of the CA concentration than 2 phf Lica 38 does exert bad influence on the surface resistivity of the composite. This phenomenon may be due to the fact that a larger amount of the CA forms a multilayer form on the surface of fillers so as to limit the transfer, thus reducing the hopping of electrons in the composite. The relationship between EMI SE and surface resistivity are shown in Figure 5, from which we can realize that a lower surface resistivity will have a higher EMI SE.

Tensile Strength

The effects of nickel-coated carbon fiber concentration on the mechanical properties of the composite are given in Figure 6. In general, a higher aspect ratio could impart a higher degree of reinforcement

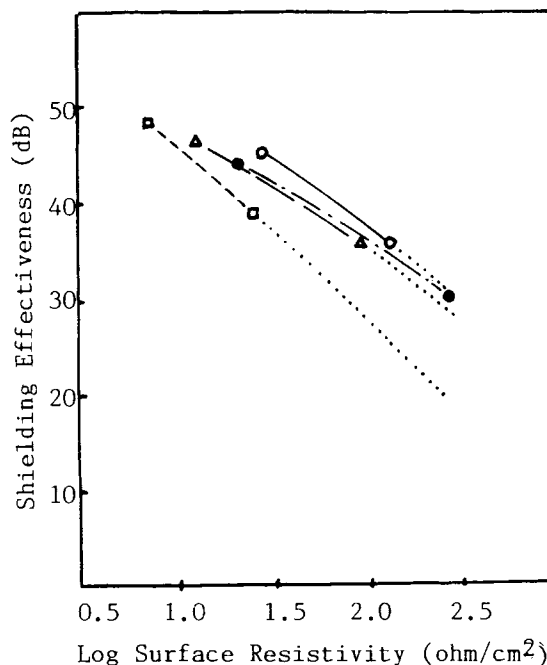


Figure 5 The relationship between SE and surface resistivity of PC-ABS (90/10%)/NCF composites, filled with (—○) 1.5 phf Ca.st., (---△) 1.5 phf Ca.st./1.5 phf Lica 38, (----□) 1.5 phf Ca.st./2.0 phf Lica 38, (—●) 1.5 phf Ca.st./2.5 phf Lica 38.

to the composite, whose physical properties would lie between those of plastics reinforced with glass fibers and those with mineral fillers, such as talc. The tensile strength declines with the increase in the loading of the fiber in the composite. The fall may result from the poor adhesion between fibers and matrices.

Another problem associated with thermoplastics, in particular, is that processing conditions during blending and compression molding lead to degradation of fibers under stress and thus lower the aspect ratio to a larger extent.

Figure 6 shows the effects of titanate CA Lica 38 on the yield stress of NCF-filled composite. The plots reveal that the yield stress decreases with the increase of NCF loading when no CA has been used. However, with the incorporation of the titanate CA, there is an improvement in yield stress. The improvement in yield stress may result from the better dispersion of NCF in the composite matrix, which, in turn, leads to better transmission of the load between the NCF and the matrix, and this can be due to greater van der Waals interaction and the presence of a higher carbon chain in this CA, which provides hydrophilicity as well as a pyrophosphate group which, being a polar group, may be providing better adhesion between NCF and the matrices.

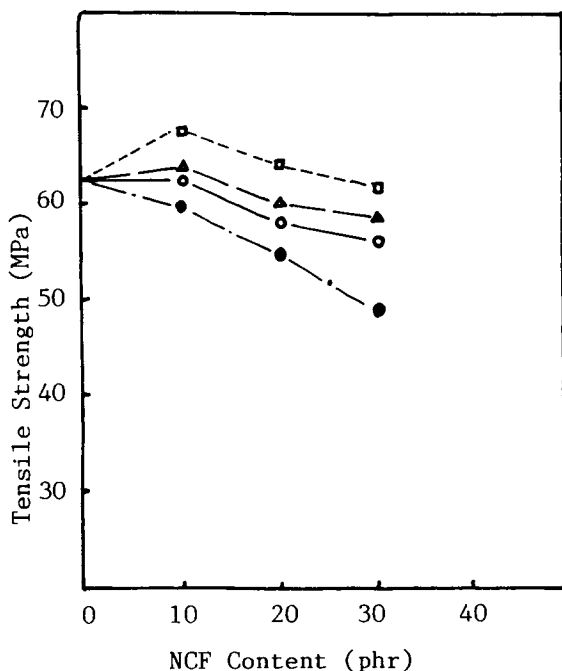


Figure 6 Tensile strength of PC-ABS (90/10%) filled with NCF, coupled with (—○) 1.5 phf Ca.st., (—△) 1.5 phf Ca.st./1.5 phf Lica 38, (---□) 1.5 phf Ca.st./2.0 phf Lica 38, (—●) 1.5 phf Ca.st./2.5 phf Lica 38.

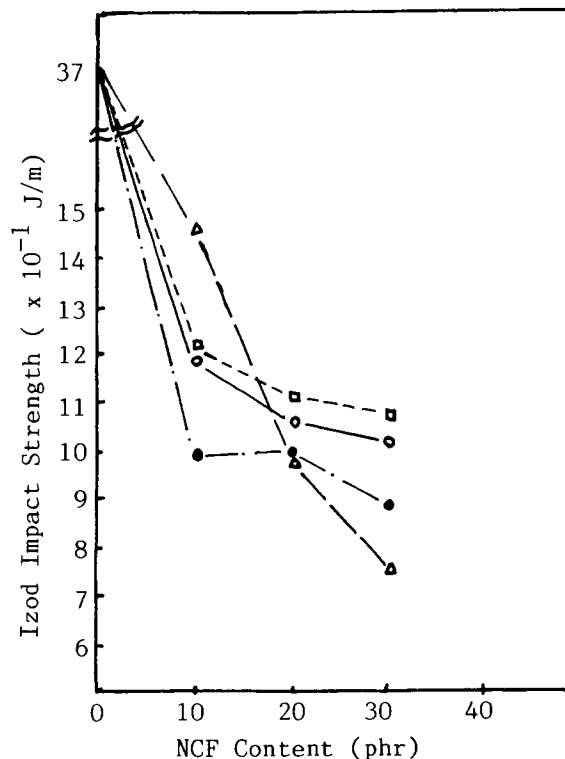


Figure 7 Notched Izod impact strength of PC-ABS (90/10%) filled with NCF, coupled with (—○) 1.5 phf Ca.st., (—△) 1.5 phf Ca.st./1.5 phf Lica 38, (---□) 1.5 phf Ca.st./2.0 phf Lica 38, (—●) 1.5 phf Ca.st./2.5 phf Lica 38.

Impact Strength

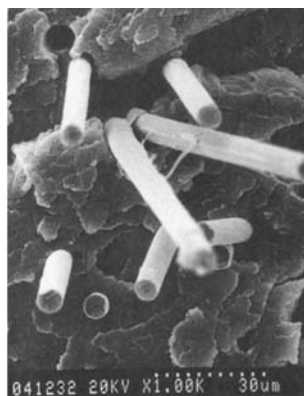
The titanate CA improves the impact strength of the NCF-filled composite with a maximum value at 10 phr fiber loading. The addition of the CA can improve the impact strength, and the best value is PC-ABS (90/10%)/2.0 phf Lica 38, as shown in Figure 7.

The increase in the impact strength with the increase in the CA concentration may be due to the plasticizing action of the CA and hence more energy is absorbed before fracture.

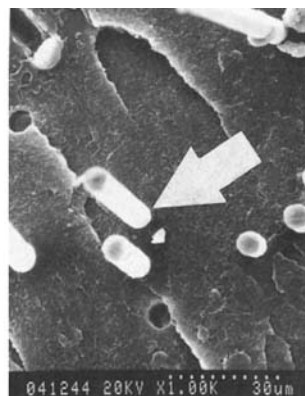
Morphology

An ABS-PC blend can be considered as a triple phase mixture of PC, Styrene-Acrylonitrile Copolymer (SAN), and butadiene rubber. The SEM micrographs of the fracture surfaces of PC-ABS blends with NCF are shown in Figure 8, where the subscripts 1, 2, and 3 represent the loading amounts 10, 20, 30 phr in the matrix and the asterisk (*) indicates that the fillers have been pretreated with 2 phf CA Lica 38.

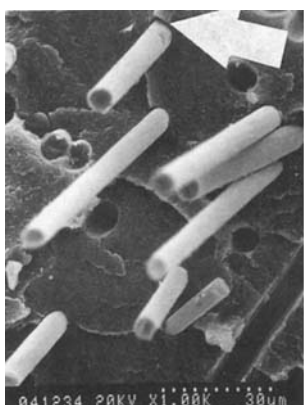
It is observed that the surface of the composite



(A1)



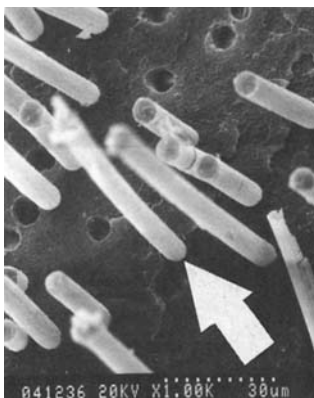
(A1*)



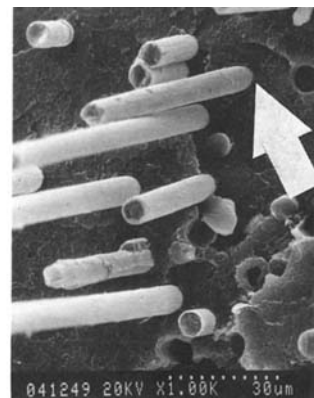
(A2)



(A2*)



(A3)



(A3*)

Figure 8 SEM photographs of PC-ABS (90/10%) filled with various NCF, (A1) 10 phr, (A2) 20 phr, (A3) 30 phr. (*) Represents NCF coupled with 2 phr titanare CA.

pretreated with CA looks more uniform than that of the composite without pretreatment. At this composition ABS as a disperse phase will be distributed in a continuous phase of PC. In addition, ABS acts as an energy absorber and improves the impact strength of this blend.

Figure 8 shows that the uncoated NCF is pulled out and has no polymer adhering to NCF; therefore, the fracture takes place at the interface. Moreover, the edge of the void is very clear, reflecting very weak adhesion interaction between the matrix and the NCF. For this reason the uncoated NCF is easily pulled out. Therefore, surface coating Lica 38 enhances the compatibility with NCF between the ABS and PC. Orientation in the Lica 38 coated system is very good, indicating the increase in impact strength. The polarity is created because of the chemical interaction between the fiber and the CA, which is an effective for improvement of the mechanical and rheological properties of the composites.

CONCLUSIONS

When the NCF was precoated with the titanate CA Lica 38, the yield stress and notched Izod impact strength increased as compared to the samples containing no CA. That indicates a better adhesion between NCF and matrices.

The optimum CA concentration for improvement in EMI SE appears to be 2.0 phf Lica 38, because the addition of CA can improve the NCF to form a better network conductive paths.

From the SEM micrographs of the fracture surfaces, it is observed that the surface of the composite pretreated with the CA looks more uniform than that of the composite not pretreated. In addition, there are more voids between fibers and matrices in the uncoated system than those in the coated system.

APPENDIX

Theory^{9,17}

Electromagnetic radiation is composed of an electric field and a magnetic field oriented at right angles to each other, both of which can induce currents in external circuit elements that happen to be within effective range as shown in Fig. A1. The nature of the wave depends on the distance (r) from source to measuring point. When $r = \lambda/2\pi$ (about one-sixth wavelength), this corresponds to the transition field condition or boundary between the near-field and far-field. When $r \gg \lambda/2\pi$ (far-field conditions), the wave impedance $Z_0 = E/H = 377 \Omega$. This is called the radiation field (plane waves).

When $r \ll \lambda/2\pi$ (near-field conditions), the ratio E/H , which is equal to the wave impedance, is not constant but depends on the characteristics of the source. If the source has low current and high voltage,

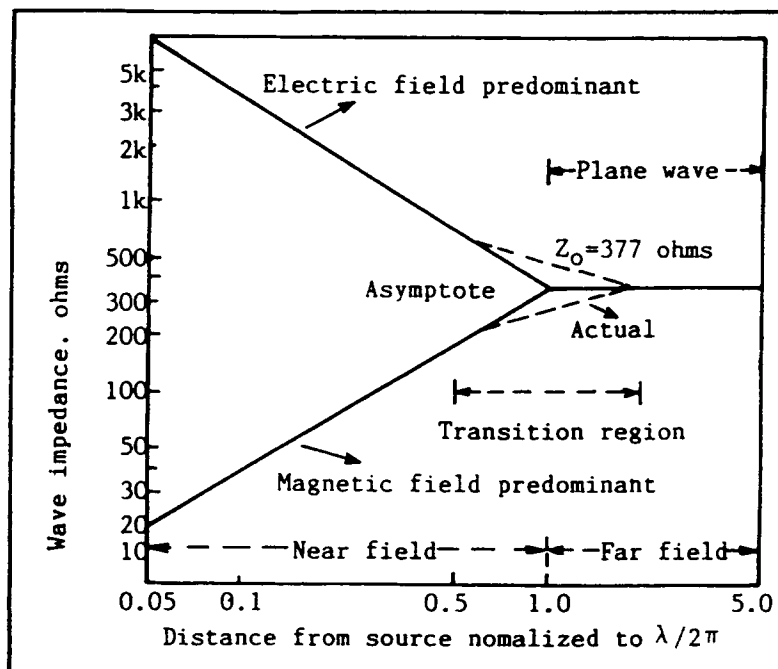


Figure A1 Wave impedance of an electromagnetic wave in the near and far fields as a function of distance from the source.⁹

the near-field will be primarily electric (E). Conversely, if the source has high current and low voltage, the near-field will be primarily magnetic (H).

The effectiveness of a shielding material is given by the logarithmic ratio of the electric (magnetic) field with and without the shield:

$$\begin{aligned} SE &= 10 \log P_i/P_t \\ &= 20 \log E_i/E_t \\ &= 20 \log H_i/H_t \end{aligned}$$

where P_t , E_t , and H_t are power, electric field strength, and magnetic field strength, respectively, of the transmitted wave and P_i , E_i , and H_i are the same properties, respectively, of the incident wave.

The shielding effectiveness (SE) can be measured with the coaxial transmission line method, which is specified in ASTM ES 7-83 or with the dual chamber method specified in ASTM ES-7. In our work the first method was used to avoid the resonance of EM wave in the dual chamber so as to decrease the experimental errors.

In passing through a shield an EM wave may be attenuated in three ways: first, by absorption (A) due to the thickness of the shield; second, by reflection (R) at the surfaces; and third, by multiple internal reflections (B) as shown in Fig. A2. The shielding effectiveness can be represented by the following expression, with all terms in dB:

$$SE(\text{dB}) = A + R + B$$

B can usually be neglected for most electric fields, plane waves (far fields), and wherever absorption losses are greater than 10 dB.

Absorption losses occur as a result of ohmic currents induced in the shield and dissipated as heat. The following equation is applicable as both near and far fields and to both electric and magnetic fields.

$$A(\text{dB}) = 3.34 t \sqrt{f_{\text{MHz}} \sigma \mu}$$

where A is attenuation in dB, t is thickness of barrier in mils (unit of 0.001 in.), f_{MHz} is frequency in MHz, σ is conductivity, relative to copper (for Cu = 1), and μ is magnetic permeability of material relative to vacuum or copper ($\mu = 1$).

From the equation it can be seen that absorption is very high at high frequencies but low at low frequencies. It increases linearly with increase in shield thickness and at a significantly lesser rate with increase in permeability and conductivity of the shield material.

The reflection loss of a plane wave, R_p , may also be calculated from

$$R_p(\text{dB}) = 108 + 10 \log(\sigma/\mu f_{\text{MHz}})$$

Compared with absorption loss, this equation indicates that the reflection loss of plane waves at low frequencies is the major attenuation mechanism. High-conductivity, low-permeability material is more effective in establishing reflection loss. As a conclusion one can say that both reflection and absorption increase with an increase in the conductivity of the material. To produce a good shield, it would therefore be effective to let the conductive fillers disperse perfectly in the shield, in order to form the infinitely conductive chain network in the composite. Now, we find that the appliance of master-batch

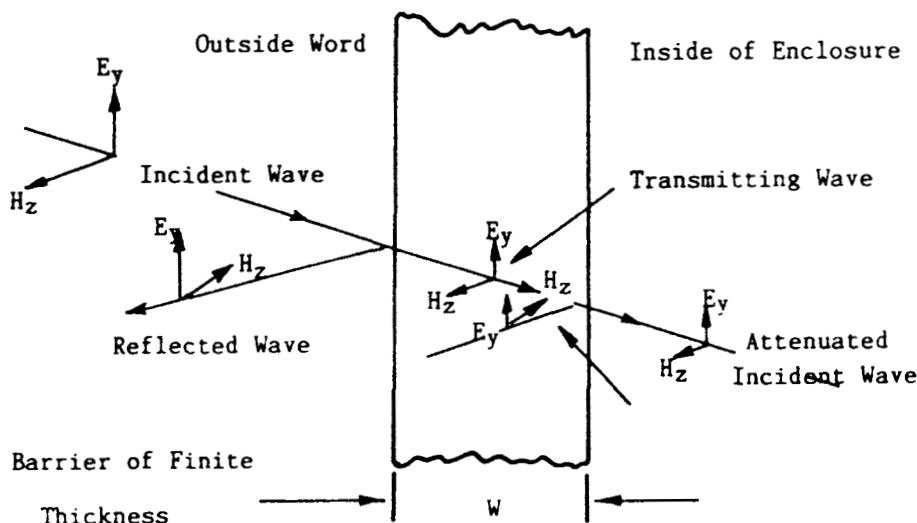


Figure A2 Shielding effect of a conductive material.⁹

method to blend and addition of a little amounts of coupling agents can obtain a good EMI shielding composite.

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