Effect of Melting Temperature, Coupling Agent, and Width on Properties of ABS+20%PC/Al Flake-Metallized Plastics

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ABSTRACT: Effects of different melting temperatures (270 and 210°C), Al flake widths (0.5 and 0.8 mm), and coupling agents (gamma aminopropyl triethoxy silane A1100 and gamma glycidoxy propyl trimethoxy silane A-187) on the properties of ABS+20%PC/Al flake-metallized plastics are discussed. According to experiments, it is found that the aspect ratio is larger with the 270°C melting temperature and 0.8 mm Al flake, but declines with the A-187 coupling agent. The 0.5 mm Al flakes treated with the A-1100 coupling agent at 270°C melting temperature has better distribution in the matrix and EMI shielding effectiveness, but has a lower volume resistance. With 0.8 mm Al flakes at 210°C melting temperature, and treatment with the A-1100 coupling agent, it produces larger ultimate tensile strength and impact strength. There is no relation between HDT and melting temperatures, Al flake widths, or coupling agents. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1902–1909, 2000

Key words: melting temperature; Al flake; coupling agent; metallized plastic; shielding effectiveness; tensile; Impact; HDT

INTRODUCTION

Electromagnetic Interference (EMI) is a type of relatively useless electromagnetic radiation caused by electric and magnetic fields. Conductance and radiation are two ways of transporting EMI.[1] When electromagnetic waves are transported to a conductive shielding, their strength intensity is decreased because of the reflection and absorption of the conduct.[2] The shielding effectiveness of the conduct is SE (dB) = R + A + M [R: consumed energy (energy losses) of the first reflection; A: consumed energy of absorption; M: consumed energy of multireflection.][3] The plastics are widely used to make shells for electronic equipment. However, those whose volume resistance is approximately 10^{17} Ω-cm cannot prevent electromagnetic interference. Therefore, making plastics conductive can help avoid electromagnetic interference. There are several methods for making plastic products conductive. They are electroless nickel plating, vacuum metallizing, metal sputtering or coating, and metallized plastics formed through adding conductive filler to the plastic.[3,4]

Conductive fillers used to form metallized plastics include (1) graphite fiber coated with nickel or copper, (2) stainless steel or copper fiber, (3) conductive carbon black, (4) metal powder, and (5) Al flake.[5,6] To compete in the computer, communication, and electronic product markets, Al flakes are preferred to produce metallized plastics. To achieve a good shielding effectiveness, a large amount of Al flakes is needed for such metallized plastics; however, in doing so, impact strength, tensile strength, and elongation will be decreased.[7,8] Besides, Gurland[9] and Malliaris and Turner[10] present data showing the resistivity of a polymer–metal composite as a function of volume loading. Because Gur-

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Table I Properties of A-187 and A-1100 Coupling Agent[20]

Couple Agent Properties	A-1100	A-187
State	Liquid state	Liquid state
Density	0.946	1.070
Boiling temperature	217°C	290°C
Molecular formula	$NH_2(CH_2)_3Si(OC_2H_5)_3$	$\overbrace{CH_2\text{—}CH}^{O}CH_2O(CH_2)_3Si(OCH_3)_3$

land's data follow the predictions up to a volume loading of about 25% conductive spheres, above this point the actual electrical conductivity goes through a transition from the low values typical of a dielectric material to values indicative of a current carrying material.[9] In addition, because a high aspect ratio tends to form conductive nets,[11,12] electrical conductivity will rise with the increase of the aspect ratio, and as a result, the content of conductive fillers can be reduced to promote mechanical properties.

The injection-molding conditions and the mold designs for metallized plastics are different from those for plastics. Lin et al.[13,14] pointed out that the rise of shielding effectiveness and electrical conductivity will increase, with the addition of conductive fillers to polyimidesiloxane (PISO). Martinsson et al.[15] indicated that if Al flakes were added to ABS, there would be an anomalous increase of Al flakes in the entrance of the mold. That is, when metallized ABS is made by injection molding, Al flakes tend to distribute in specific orientation in the entrance of the mold, within which the anisotropy conductivity rises with the increase of Al flake content. Then, Bell et al.[16] reported that a coupling agent could increase the adhesive strength between polymer and metal. Wu et al.[17] found that a silane coupling agent with different molecular structures will affect mechanical properties of the composite. The interface between plastic and Al flakes will multiply with a rise in the aspect ratio, and cause the degradation of mechanical properties of metallized plastic. Tanagawa et al.[18] indicated that the flexural modulus of ABS/aluminum fiber and brass fiber would rise by increasing the content of conductive fillers, but the tensile strength and maximum elongation, on the contrary, will be decreased. Furthermore, by using a scanning electron microscope to observe the tensile fracture morphologies, it is found that the bonding of plastic and fiber is relatively poorer. Chen and Ma[7] found in their study of mixing ABS, carbon black, and the Al flake process, that the viscosity becomes much higher under a low shear rate, and the tensile strength and impact strength are reduced by increasing the content of carbon black and Al flakes. Bigg[8] pointed out that if polypropylene (PP) is metallized with Al fiber, its tensile strength will reduce because of the weaker bonding strength between the Al fiber and plastic.

This research has explored a new metallized plastic, ABS+20wt%PC/Al Flake [the aluminum flake was dispersed into acrylonitrile–butadiene–styrene (ABS) and 20 wt % polycarbonate (PC): the ABS/PC blend], and then the effects of different melting temperatures, coupling agents, and widths of the Al flake on the properties of the metallized plastics are discussed.

EXPERIMENTAL

Metallized Plastic Pellet Preparation

Flame-retardant grade ABS+20 wt % PC produced by American GE corporation was used as the plastic matrix, and 1100 Aluminum (0.5 mm in length ×18 μm in thickness, and 0.8 mm × 18 μm) was employed as the conductive filler. Two kinds of coupling agents, Union Carbide® Organofunctional (gamma aminopropyl triethoxy silane (A-1100), and gamma glycidoxy propyl trimethoxy silane (A-187), whose characteristics are shown in Table I, were used in this experiment. Aluminum strips were immersed in the two coupling agents after grease on the strips was eliminated with acetone. Then aluminum strips were dried off after the surfaces have been well covered with coupling agent. Through the extruder with a T-mode head, the covered plastic rods were formed and cut into metallized plastic pellets containing 27 wt % Al flakes, and having a length of 7 mm and a diameter of 3 mm after passing through the cooling system. Consequently, three kinds of metallized plastic pellets were prepared: (1) an aluminum strip covered with the A-187, (2) an aluminum strip covered with the A-1100, and (3) an aluminum strip without covering with any coupling agent.

Injection Molding

Metallized plastic particulate was kept in a drying oven of 110°C for 4 h to reduce the content of water to lower than 0.04%. The parameters of the injection molding were 30% (94 L/h) in injection speed, 32 rpm in screw speed, 100 bar in injection pressure, 30 bar in holding pressure, 80°C in mold temperature, and 270 and 210°C in melting temperature.

Al Flake Extraction

The plastic matrix was kept in an air furnace of 510 ± 3°C for 2 h, and then put in an acetone system to remove the plastic matrix. The length of the extracted Al flakes was observed through a Yashica RFB-7 stereomicroscope to obtain the average aspect ratio. Each average aspect ratio value was the average of at least 10 measurements.

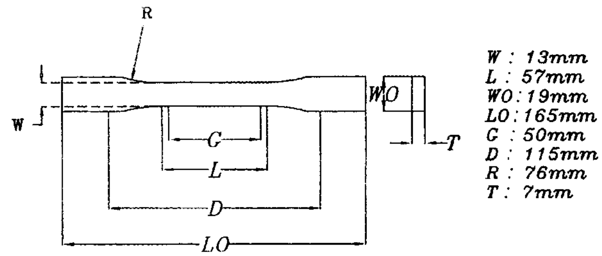
Property Tests

With frequencies from 30–1350 MHz, shielding effectiveness was measured by an ASTM D4935-89 Coaxial Transmission Test.

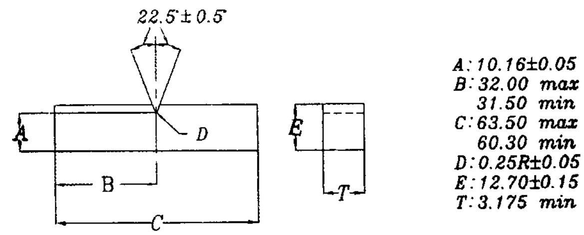
The volume and surface resistivity were measured using specimens 13.5 mm in diameter and 3.3 mm thick according to ASTM D257. Volume resistance (ρ_v) was obtained through the formula, ρ_v = A Rv/t (ohm-cm) and A = $(D_1 + g)^2\pi/4$; surface resistance (ρ_s), through ρ_s = p Rs/g (ohm per square) and p = πD_0, where Rv is the measured volume resistance; Rs is the measured surface resistance; A is the electrode area; P is the electrode perimeter; t is the specimen thickness; D_1 is the inner diameter; D_0 is the outer diameter; g is the $D_0 - D_1$.

Based upon the standards of ASTM D638, shown in Figure 1(a), dumb bell specimens are made to test the tensile strength with the Instron tensile testing machines at room temperature and a 5 mm/min crosshead speed.

Based on the standards of ASTM D256, shown in Figure 1(b), impact-testing specimens with a



(a)



(b)

Figure 1 Standards of the (a) tensile and (b) impact specimen.

thickness of 1/8″ are made. The impact test progresses at room temperature by using an Izod type notched head.

In accordance with ASTM D64, heat distortion temperature (HDT) is surveyed with standardized specimen (127 × 7 × 13 mm). First, both ends of the specimen are settled on two props. Then, a fixed bending moment of 1.46 kg is put on the middle of the specimen, which is simultaneously heated, with a heat rate of 2 ± 0.2°C. When the deflection of the specimen is up to 0.254 mm, the specific temperature is measured.

Each property value mentioned above was the average of at least three measurements.

Microstructure Observation

After being ground with 1200 grit carbimet paper, the surface of produced metallized plastics is polished with a dense 0.05 μm Al_2O_3 slurry. Then, an OPTIPHOT-110 Nikon optical microscope is used to observe the distribution of Al flakes in the matrix. In addition, fracture morphologies of impact and tensile tests are observed, with a JEOL-JSM840A scanning electron microscope (SEM) after 2-min gold plating of the fracture side.

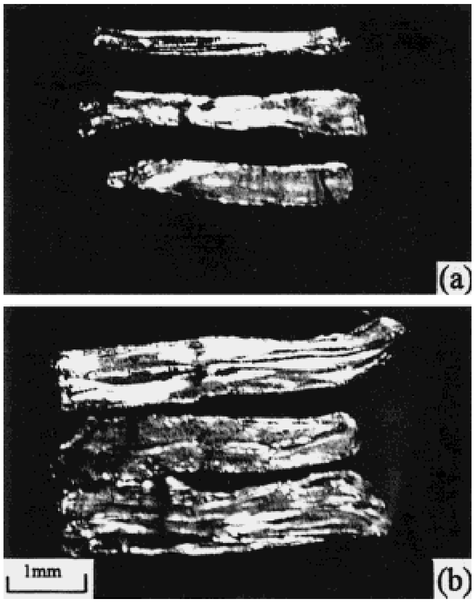


Figure 2 OM photograph for the aspect ratio of (a) the 0.5 mm and (b) the 0.8 mm Al flake without treatment with a coupling agent at 270°C melting temperature.

RESULTS AND DISCUSSION

Aspect Ratio

Before injection molding, the aspect ratio of Al flake of ABS+20 wt% PC/Al flake metallized plastic is 388. After injection molding, the extracted Al flakes are shown in Figure 2, and the aspect ratio of 0.5 and 0.8 mm Al flakes treated with different melting temperatures and different coupling agents are shown in Table II. The aspect ratio is calculated from the measured average lengths of the Al flakes and a constant thickness of the Al flakes at 18 microns. The cause of aspect ratio decrease is found. In the process of injection molding, flakes are broken and cut in the screw feeding zone, metering zone, compression zone, and the gate, and the strength of Al flake is not strong enough to bear the shear stress, consequently resulting in the reduction of Al flake lengths. Besides, the melting temperature at 210°C produces a higher viscosity and shear stress than at 270°C, and the lower melt temperature tends to cause a lower aspect ratio of the Al flake. The bonding of the Al flake and plastic with the A-1100 coupling agent is weaker than with the A-187 coupling agent; therefore, its shear stress will not fracture the Al flakes easily, and as a result, achieve a higher aspect ratio. Then, the Al flake, with a width of 0.8 mm, has a higher aspect ratio than that of 0.5 mm. Here, one thing is worth mentioning. The aspect ratio of metallized plastics designed in this study is larger than other commercial products.

Table II Aspect Ratio of Different Melting Temperatures, A1 Flake Widths, and Coupling Agents

Width of A1 Flake (mm)	Coupling Agent	Aspect Ratio	
		210°C	270°C
0.5	non	—	186 ± 10
	A-187	136 ± 12	175 ± 7
	A-1100	164 ± 6	182 ± 7
0.8	non	—	233 ± 15
	A-187	188 ± 14	214 ± 12
	A-1100	211 ± 10	230 ± 10

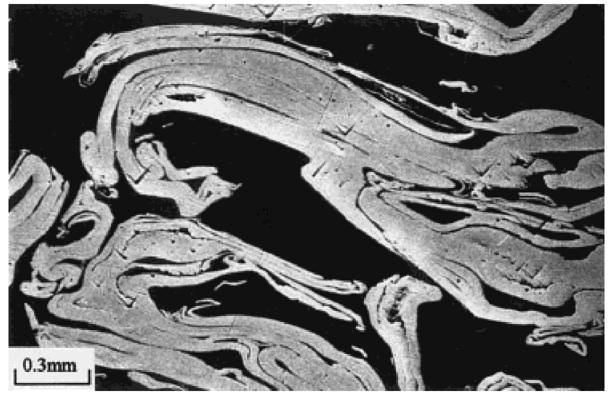


Figure 3 OM photograph for the distribution of the Al flakes in the shot.

The Distribution of Al Flakes in Shot, Gate, and Matrix

The distribution of Al flakes in the shot is shown in Figure 3. It is found that Al flakes apparently cluster in the shot. In the melting flow, it is more difficult for Al flakes to become deformed than melted plastic, and Al flakes are inclined to pile up in the shot; besides, Al flakes at widths of 0.5 and 0.8 mm are much thicker than 18 μm, which is apt to make the Al flakes pile up face to face, forming layer clustering. The distribution of Al flakes in the gate is shown in Figure 4, from which it is found that the degree of clustering is lower than in the shot. This is because the melting flow in the gate is less impeded than in the

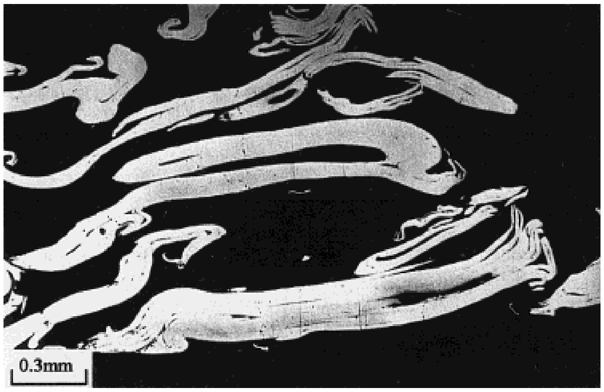


Figure 4 OM photograph for the distribution of the Al flakes in the gate.

shot. The distribution of Al flakes in the matrix is shown in Figure 5. There is a stronger bonding between the Al flakes and plastic treated with the A-187 coupling agent, and several pieces of Al flakes pile up face to face, as shown in Figure 5(a)–(c). Then, because of the weaker bonding between the Al flakes and plastic treated with the A-1100 coupling agent, Al flakes are distributed more homogeneously in the matrix. The distribution of 0.5 mm Al flakes in the matrix is more uniform than 0.8 mm Al flakes in the matrix.

Volume Resistance and EMI Shielding Effectiveness

The volume resistance of different melting temperatures, Al flake widths, and coupling agents is shown in Table III. It is found that volume resistance will be lower if the surface of the Al flakes is treated with the A-1100 coupling agent at a melting temperature of 270°C or without the coupling agent than treated with the A-1100 (210°C), A-187 (210°C and 270°C). The reason is that the coupling agent treated with the Al flakes may render the Al flakes surface nonconductive. This insulates neighboring flakes in the network increasing the bulk resistance of the system. Because electron hopping is an exponential function of distance, small changes in the interflake electrical gap can have effects on the volume conductivity of the composite structure. However, the volume resistance is lower when Al flakes are treated with the A-1100 coupling agent, whose boiling point is 217°C, at a melting temperature of 270°C, because depolymerization of the coupling agent will occur on the Al flake surface. At 210°C, using the A-187 coupling agent we can achieve a lower volume resistance than using the A-1100. It is worth mentioning that the volume resistance of metallized plastic is measured according to ASTM D257. Errors often occur in measuring, because the flakes turn over and over easily in the melted plastic. Al flakes pile up face to face (with the A-187 coupling agent) with more chances to contact or overlapped each other than distribute uniformly (with the A-1100 coupling agent) vertically in the direction of the thick side. Then, an electric conductive path is formed among the upper metallic pole and the overlapped or contacted Al flakes and the bottom metallic

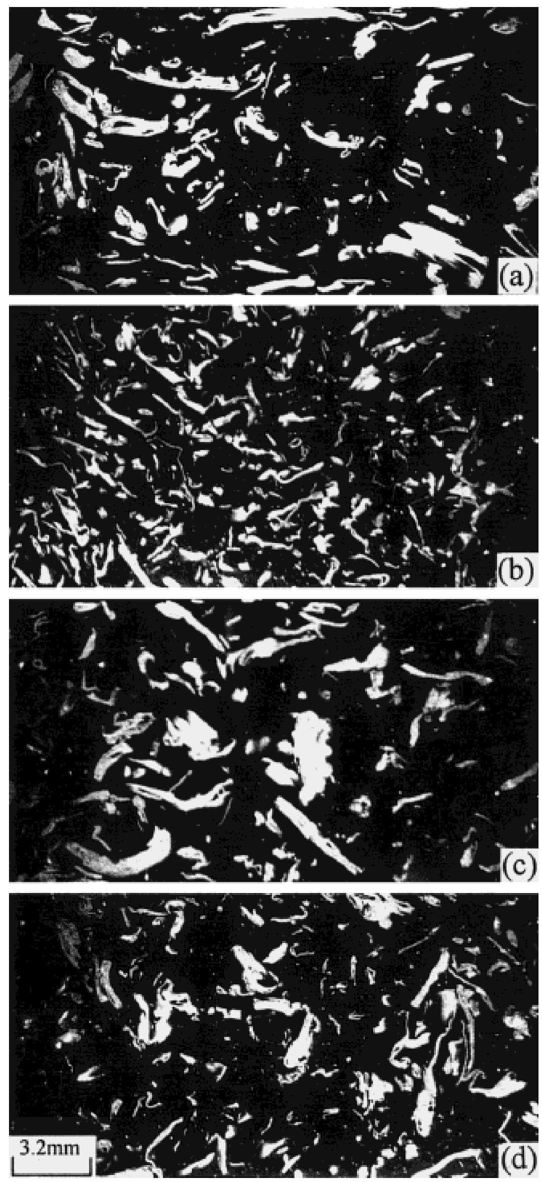


Figure 5 OM photograph for the distribution of the 0.5 mm Al flakes at (a) A-187/270°C, and(b) A-1100/270°C, and of 0.8 mm Al flakes at (c) A-187/270°C, (d) A-1100/270°C in the matrix.

Table III Volume Resistance of Different Melting Temperatures, A1 Flake Widths, and Coupling Agent

Width of A1 Flake (mm)	Coupling Agent	Volume Resistance (ohm-cm) 210°C	270°C
0.5	non	—	44.3 ± 2.8
	A-187	118.5 ± 7.67	138.4 ± 9.7
	A-1100	155.6 ± 10.6	37.8 ± 2.7
0.8	non	—	39.5 ± 2.6
	A-187	127.1 ± 7.5	139.6 ± 10.2
	A-1100	168.6 ± 11.9	43.7 ± 3.2

pole decrease volume resistance of the metallized plastic. However, the volume resistance or surface resistance of the other area, besides the overlapped or contact Al flakes in metallized plastic, still have a high value of volume resistance or surface resistance. The A-1100 coupling agent, on the contrary, has a higher volume resistance, because the Al flakes tend to be distributed homogeneously in the plastic, and reduces the chances of contacting each other when moving vertically in the direction of the thick side. The volume resistance of the 0.5 mm Al flakes is lower than that of the 0.8 mm Al flakes, because its contact in the direction of the thickness side is better.

Shielding effectiveness in the frequency from 30–1350 MHz of different Al flake widths, melt temperatures, and coupling agents is shown in Figure 6. With lower volume resistance, the Al flakes treated with or without the A-1100 coupling agent at 270°C have higher shielding effectiveness between 52 and 25 dB in the low frequency from 30–300 MHz, and then it is between 21 and 25 dB in the high frequency from 300–1350 MHz. Because of the low aspect ratio of the Al flakes treated with the A-187 coupling agent, the clustering pieces tend to turn over in the melting flow to cause the Al flakes to be distributed at various angles, which is attributed to multireflection in the low frequency. Nevertheless, because it is hard to form a conductive network, the shielding effectiveness is smaller in the higher frequency. Owing to the lower volume resistance and better distribution, the shielding effectiveness of the 0.5 mm Al flakes is better than that of the 0.8 mm.

Impact Strength

The impact strength of different Al flake widths, coupling agents, and melting temperatures is

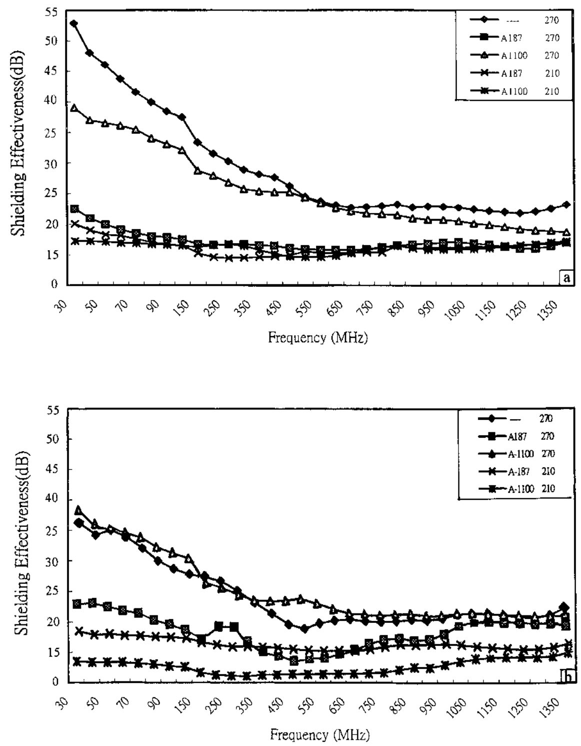


Figure 6 The effects of different melting temperatures, coupling agents, and Al flake widths (a) 0.5 mm (b) 0.8 mm on the frequency of electromagnetic waves.

shown in Table IV. Due to the strong bonding strength of the A-187 coupling agent, the Al flakes are apt to crack directly, as shown in Figure 7(a)–(c). Because of the weak bonding strength of the A-1100 coupling agent, some Al flakes are pulled out in the fracture morphologies, as show in Figure 7(b)–(d), and the cracks are prone to progress along the interface of the Al flakes and the matrix to prolong the path of cracking. At a melting temperature of 210°C, good distribution of the Al

Table IV Impact Strength of Different Melting Temperatures, A1 Flake Widths, and Coupling Agent

Width of A1 Flake (mm)	Coupling Agent	Impact Strength (J/m) 210°C	270°C
0.5	non	—	113.6 ± 7.6
	A-187	136.7 ± 8.7	118.6 ± 7.2
	A-1100	153.9 ± 10.2	115.6 ± 9.4
0.8	non	—	95.2 ± 4.7
	A-187	159.5 ± 11.5	94.5 ± 4.0
	A-1100	179.5 ± 13.7	97.1 ± 7.8

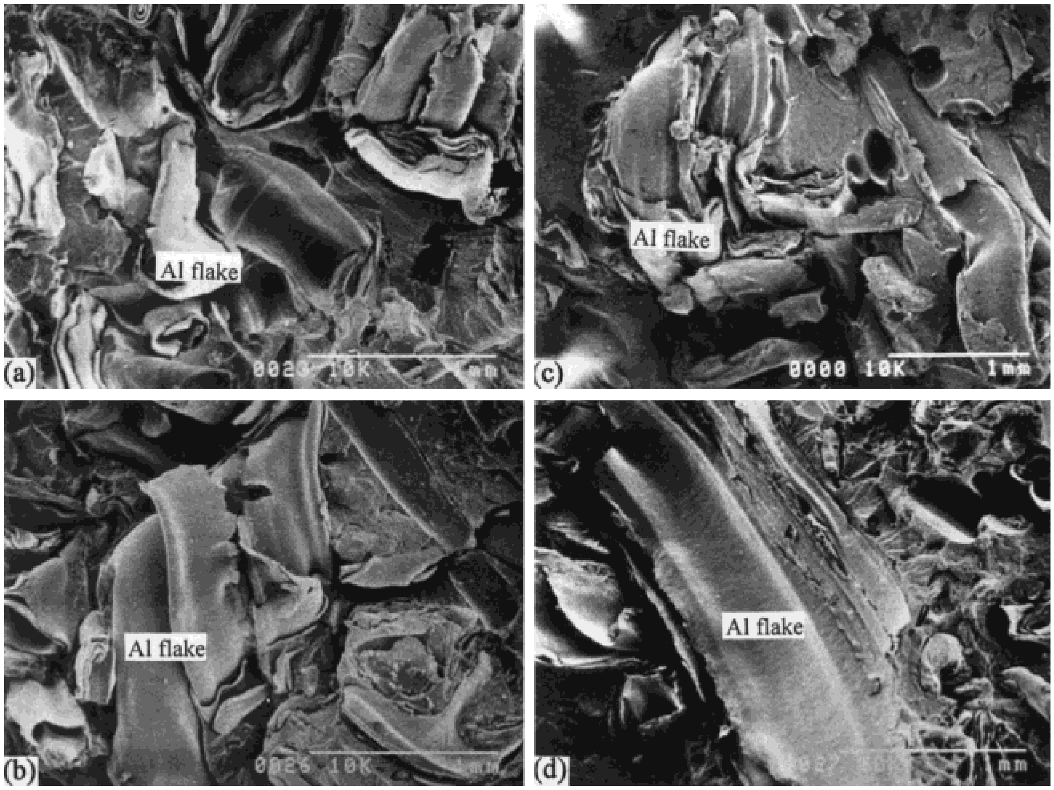


Figure 7 SEM photographs of fracture morphologies for impact tests of (a) the 0.5 mm Al flake at A-187/210°C, (b) the 0.5 mm Al flake at A-1100/210°C, (c) the 0.8 mm Al flake at A-187/210°C, and (d) the 0.8 mm Al flake at A-1100/210°C.

flakes with a lower aspect ratio in the matrix can prevent the growth of cracks, and then promote impact strength. On the contrary, the temperature of 270°C will degrade the mechanical properties of polymers and cause a decrease in impact strength.

Ultimate Tensile Strength and Heat Distortion Temperature

The ultimate tensile strength of different coupling agents, Al flake widths, and melting temperature is shown in Table V. The contribution of the matrix plastic deformation to the metallized plastic ultimate tensile strength also critically depends on the Al flake/matrix adhesion and Al flake width. Ultimate tensile strength is better when the melting temperature is at 210°C, for its lower depolymerization of the coupling agent increases the adhesion opportunities of the Al flake with plastic, and it is found that the Al flakes crack directly, owing to the fact that the tensile strength of the matrix is larger than the Al flake, and the matrix area of the 0.8 mm Al flakes is larger than the 0.5 mm Al flakes. Thus, the ultimate tensile strength of the 0.8 mm Al flakes is better than the 0.5 mm Al flakes at 210°C. On the other hand, at 270°C melting temperature, depolymerization of the matrix and will cause a decline in matrix plastic deformation, and the cracks or crazes are easily produced in the matrix.

Table V Ultimate Tensile Strength of Different Melting Temperatures, Al Flake Widths, and Coupling Agents

Width of Al Flake (mm)	Coupling Agent	Ultimate Tensile Stress (MPa)	
		210°C	270°C
0.5	non	—	33.0 ± 1.6
	A-187	39.2 ± 2.0	36.1 ± 2.0
	A-1100	39.7 ± 1.5	34.9 ± 1.4
0.8	non	—	34.6 ± 1.8
	A-187	41.8 ± 1.5	36.6 ± 2.0
	A-1100	44.2 ± 2.1	34.0 ± 1.5

Thus, the ultimate tensile strength is independent of the Al flake widths or coupling agent.

HDT, which is about 132 ± 1°C, has no relation to melting temperature, coupling agent, or Al flake widths.

CONCLUSIONS

The effects of melting temperatures (270 and 210°C), Al flake widths (0.5 and 0.8 mm), and coupling agents [gamma aminopropyl triethoxy silane (A-1100) and gamma glycidoxy propyl trimethoxy silane (A-187)] on the properties of ABS+20%PC/Al Flake metallized plastics are discussed, and the conclusions are as follows: (a) the apect ratio is increased with a rise in melting temperature and of Al flake width, but it is reduced with the A-187 coupling agent; (b) Al flakes distribute well in the matrix, but cluster in the shot and gate. The 0.5 mm Al flakes treated with the A-1100 coupling agent at 270°C melting temperature have better distribution. But, 0.8 mm Al flakes, and treated with A-187 coupling agent tend to cluster as pieces in matrix; (c) 0.5 mm Al flakes treated with or without the A-1100 coupling agent at 270°C melting temperature have lower volume resistance and better EMI shielding effectiveness; (d) 0.8 mm Al flakes treated with the A-1100 coupling agent at 210°C melting temperature have better impact strength and ultimate tensile strength.

There is no relation between HDT and melting temperatures, Al flake widths, or coupling agents.

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