JOURNAL OF MATERIALS SCIENCE **34** (1999) 1461 – 1470

Polymer microlayer structures with anisotropic conductivity

S. NAZARENKO, A. HILTNER, E. BAER
Department of Macromolecular Science, and Center for Applied Polymer Research, Case Western Reserve University, Cleveland, OH 44106-7202,USA

Continuous layer-multiplying coextrusion offers a new approach for processing metal-filled polymers into conducting structures. In this process, filled and unfilled polymers are combined into unique structures with many alternating layers of two or more components. The total number of layers can range from tens to thousands. The ability of microlayering to "organize" anisotropic particles was used to obtain metal-filled polypropylene tape with highly anisotropic electrical properties. Orientation of metal flakes by microlayering increased the anisotropy in resistivity by two orders of magnitude over compression molding. Isolation of individual filled layers by alternating filled and unfilled layers resulted in materials with many independent conducting pathways. Filled layers with 10% (v/v) copper flakes or 15% (v/v) nickel flakes were conductive only if the filled layers were thick compared to the thickness of the flake particles. When the thickness of the filled layers approached the particle thickness, the conductive properties were lost. This behavior was understood by comparing the three-dimensional arrangement of flakes in thick conductive layers with the two-dimensional particle layout of thin non-conductive layers. © *1999 Kluwer Academic Publishers*

1. Introduction

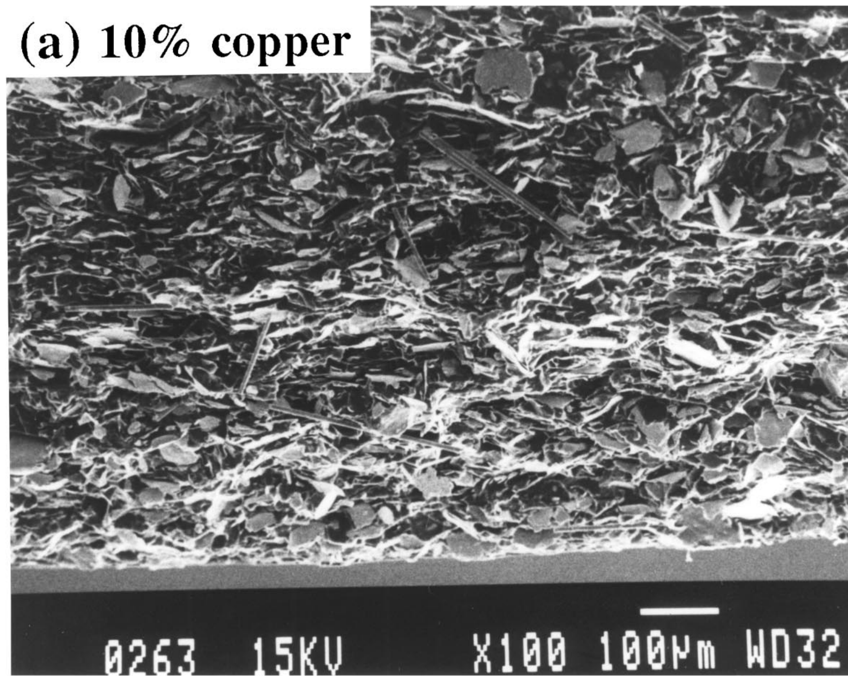
Interest in conductive plastics has been stimulated by the numerous opportunities afforded by the rapidly developing electronics industry, particularly for EMI shielding, in low temperature heaters, and as transducers. Although most polymers are insulators, conductive properties can be achieved by blending with a metal filler [1–3]. Metal-filled polymers undergo a sharp transition from an insulator to a conductor at a critical filler concentration. The sharp change is due to the formation of a network among the conducting filler particles. This network does not necessarily imply physical contact between adjacent particles; hopping or tunneling, i.e. the processes by which an electron jumps across an insulator gap, can also produce the network. Network formation is frequently treated as a percolation process [2, 4].

Dispersions of spherical particles typically require a volume fraction between 0.20 and 0.40, depending on size distribution, to achieve electrical conductivity [5–7]. Dimensionally oriented filler particles (flakes and fibers) induce conductivity in a random dispersion at much lower concentrations than spherical particles or irregular particles having an aspect ratio of 1 [3, 8, 9]. The critical volume fraction, typically in the range of 0.10, strongly depends on the aspect ratio.

An alternative approach for reducing the volume concentration of conductor is to segregate the conductive filler from the matrix into a conducting network. This approach relies on special processing techniques to form conductive paths through the matrix. For example, ferromagnetic particles have been aligned in a magnetic field, although this requires a low viscosity thermosetting matrix to permit particle alignment and connectivity [10]. Alternatively, polymer particles have been coated with metal [11–13] and the mixture compression molded or compaction-sinter molded in a way that the polymer does not flow enough to disrupt the metal particle network. A segregated polymer network has also been obtained by taking advantage of the natural segregation of submicron filler particles in semicrystalline polymers and phase-separated blends [14, 15].

Continuous layer-multiplying coextrusion offers a new approach for processing metal-filled polymers into conducting structures. In this process, filled and unfilled polymers can be combined into unique structures with many alternating layers of two or more components [16–18]. Typically, the total number of layers ranges from tens to thousands. The submicron layer thicknesses can be precisely controlled by varying the melt feed ratio, the final sheet or film thickness, and the number of layers. If the filler particles are anisotropic, for example platelets, flakes, or short fibers, the geometric constraints imposed by layer multiplying promote orientation of the particles in the plane of the layers. The advantages of microlayering include the ability to process many thermoplastic matrices with almost any type of filler.

In the present study, the ability of microlayering to "organize" anisotropic particles was used to obtain metal-filled microlayered polypropylene tape with highly anisotropic electrical properties. Individual filled layers



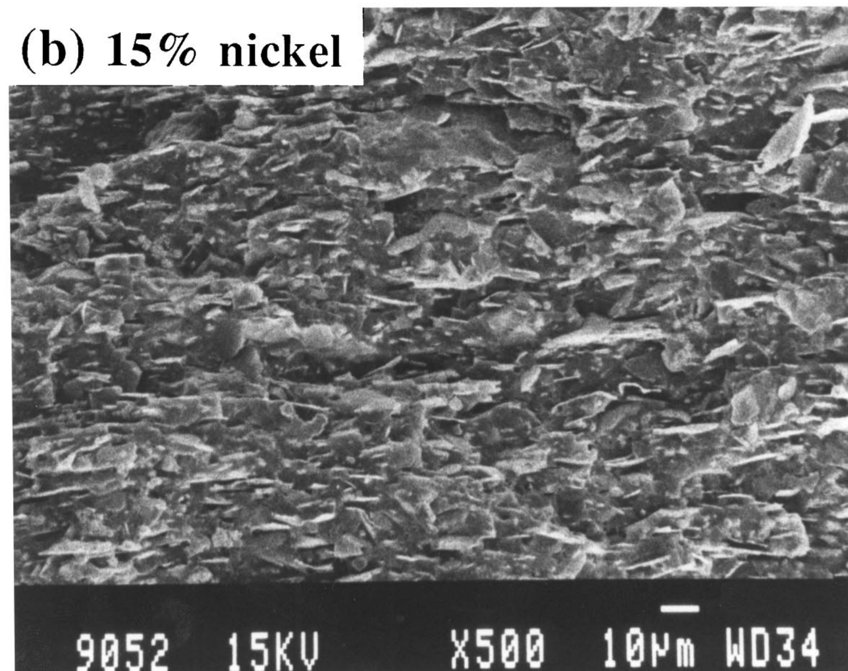


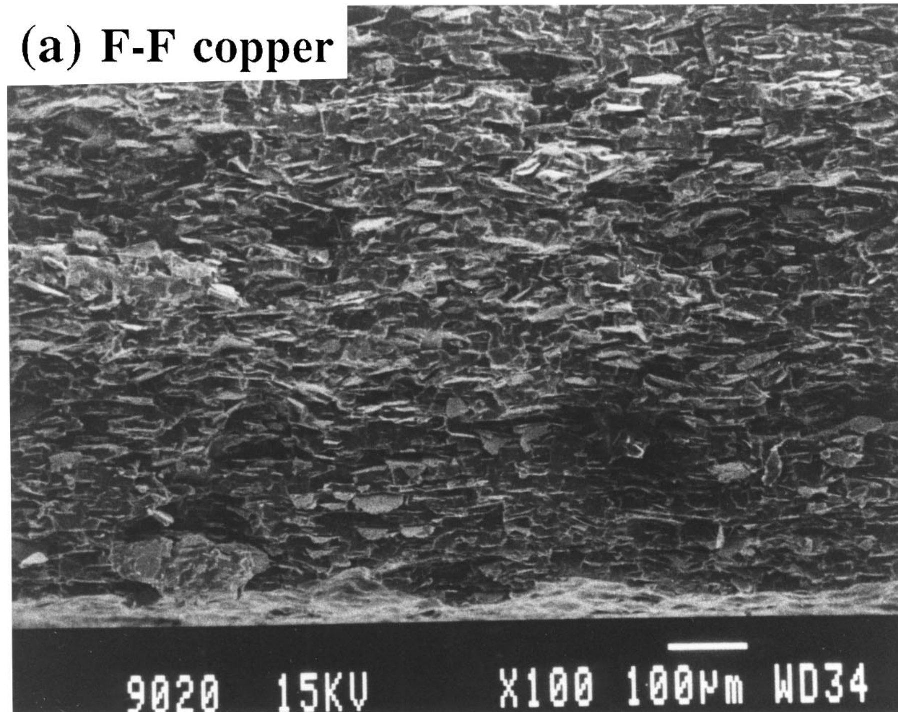
Figure 1 Scanning electron micrographs of compression molded, metal-filled polypropylene: (a) 10% (v/v) copper; and (b) 15% (v/v) nickel.

were isolated from each other by alternating filled and unfilled layers. In this configuration, it was anticipated that conductivity would follow many independent pathways through the interior of the tape. The study focused on the effect of layer thickness and composition on the anisotropic conductive behavior of the new materials.

2. Experimental

The polypropylene was Pro-Fax 6523 supplied by Himont Co. Silver-coated copper flakes with an average thickness of 3 μm and average aspect ratio of 15 were obtained from Degussa Co. Nickel flakes with an average thickness of 1 μm and average aspect ratio of 10 were obtained from Novamet, Wyckoff, NJ. Blends of polypropylene with 2.5, 5, 7.5, 10, 12.5, 15 and 20% (v/v) silver-coated copper flakes and with 5, 10, 15, 20 and 25% (v/v) nickel flakes were prepared in a Haake Rheometrix 600 by mixing at 190 °C for 8 min at 60 rpm under dry nitrogen. The blends were compression molded into 2 mm thick plaques at 190 °C.

Two types of microlayers were extruded using the methodology described previously [17,18]. Microlayers with 128 layers were coextruded with filled polypropylene in both extruders (F-F microlayers). This type of microlayer was prepared from the blend with 10% copper and from the blend with 15% nickel. Additional microlayers were prepared with layers of unfilled polypropylene alternating with layers of filled polypropylene in a 1 : 1 ratio (U-F microlayers). This type of microlayer was prepared with 8, 16, 64 and 128 layers using the blend with 10% copper, and with 64,



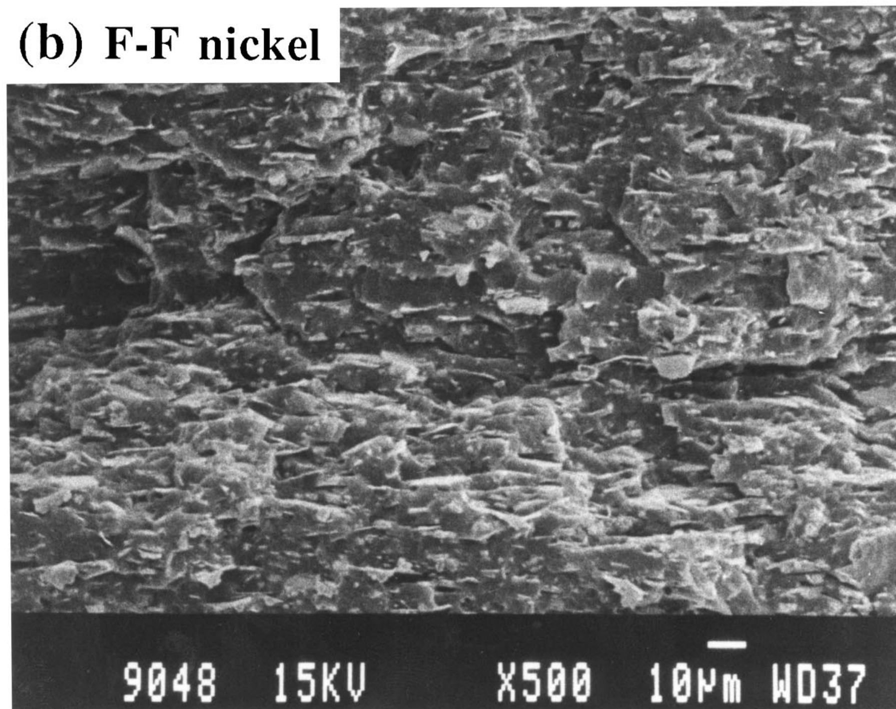


Figure 2 Scanning electron micrographs of F-F microlayers: (a) 10% (v/v) copper-filled polypropylene with 128 layers; and (b) 15% (v/v) nickel-filled polypropylene with 128 layers.

128 and 256 layers using the blend with 15% of nickel. A control was prepared by microlayering polypropylene with 128 layers. The overall microlayer tape thickness was about 1 mm.

The metal filler content after microlayering was determined by thermogravimetric analysis using a Perkin-Elmer 7 TGA. The particle orientation and distribution within the layers and in the compression molded blends was carried out using a scanning electron microscope (JEOL JCM 840A). To observe the layer morphology and particle distribution and orientation, the microlayers were cryogenically fractured through the cross-section and coated with 90 Å of gold.

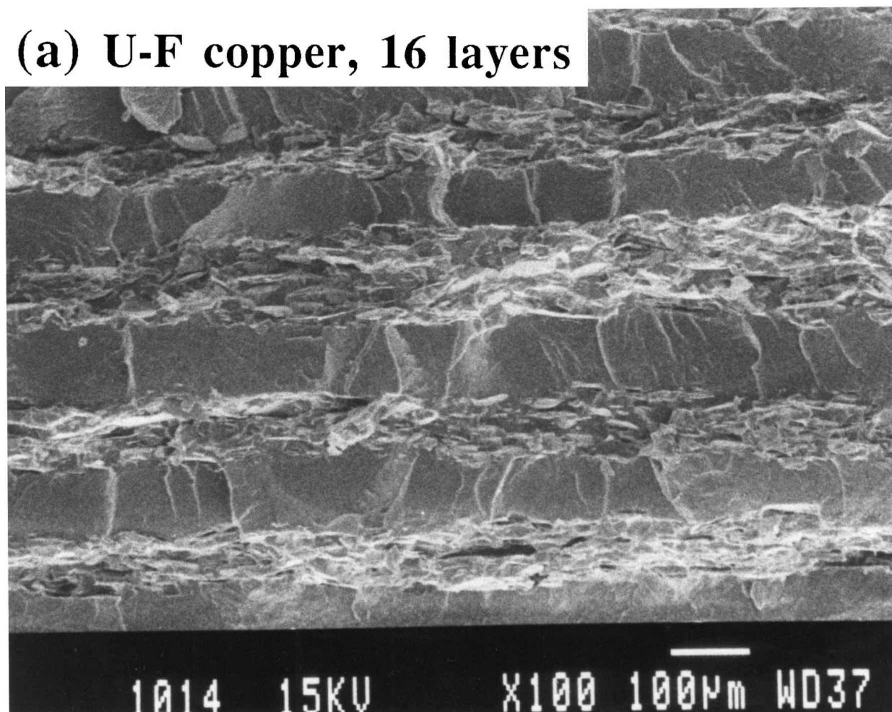
To measure resistivity, contact faces were polished and a 1000 Å gold layer was deposited for a good electrical contact with the polymer surface. The contacts were applied either to the surfaces of the plaque or tape to measure the cross-plane resistivity, or to the edges to measure the in-plane resistivity. The contact area was about 4 cm^2 for specimens taken from compression molded plaques, and 0.3 cm^2 for both cross-plane and in-plane configurations of the microlayers. Voltage was applied through conductive tape contacts attached to the contact faces. This procedure gave good electrical contact and eliminated the need to apply pressure to the specimen. This was an important feature of

the specimen design because application of pressure to metal-filled polymers in order to obtain good contact can significantly alter the measured resistivity [19]. The experimental setup used to measure the volume resistivity consisted of a power supply as a voltage source and an electrometer (Keithley 616) to measure electrical current through the sample as a function of the applied voltage. All conductors were isolated with Teflon standoffs. The specimen surface temperature was continuously monitored during the voltage-current measurements. A temperature rise of no more than 2–3 °C at the maximum applied voltage was allowed.

3. Results and discussion

3.1. Structure of compression molded blends and microlayers

The two micrographs in Fig. 1a and b shows compression molded blends of PP filled with 10% copper and 15% nickel. Different magnifications are shown because the copper particles with average thickness 3 μm and average diameter 45 μm were substantially larger than the nickel flakes with average thickness 1 μm and average diameter 10 μm. The particles in both blends were well-dispersed and were noticeably oriented in the plane of the compression molded plaque. It is known



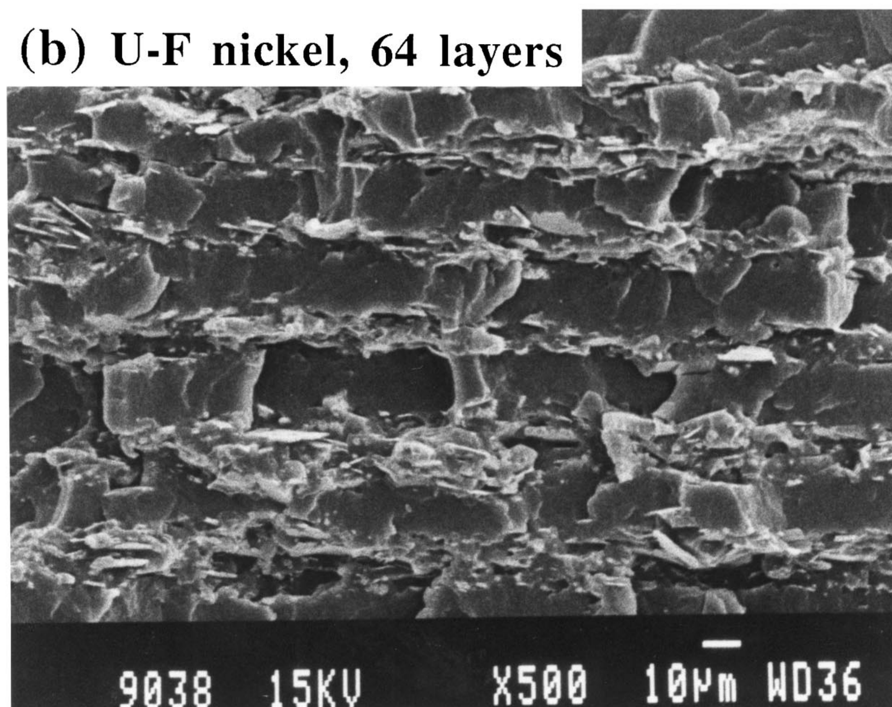
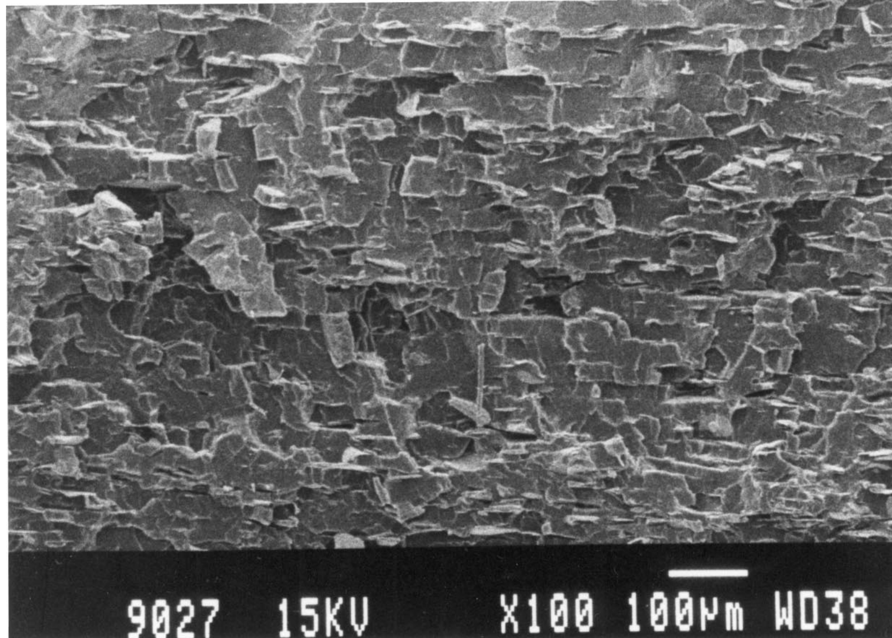


Figure 3 Scanning electron micrographs of U-F microlayers with thick layers: (a) Alternating 10% (v/v) copper-filled polypropylene and unfilled polypropylene with 16 layers; and (b) alternating 15% (v/v) nickel-filled polypropylene and unfilled polypropylene with 64 layers.



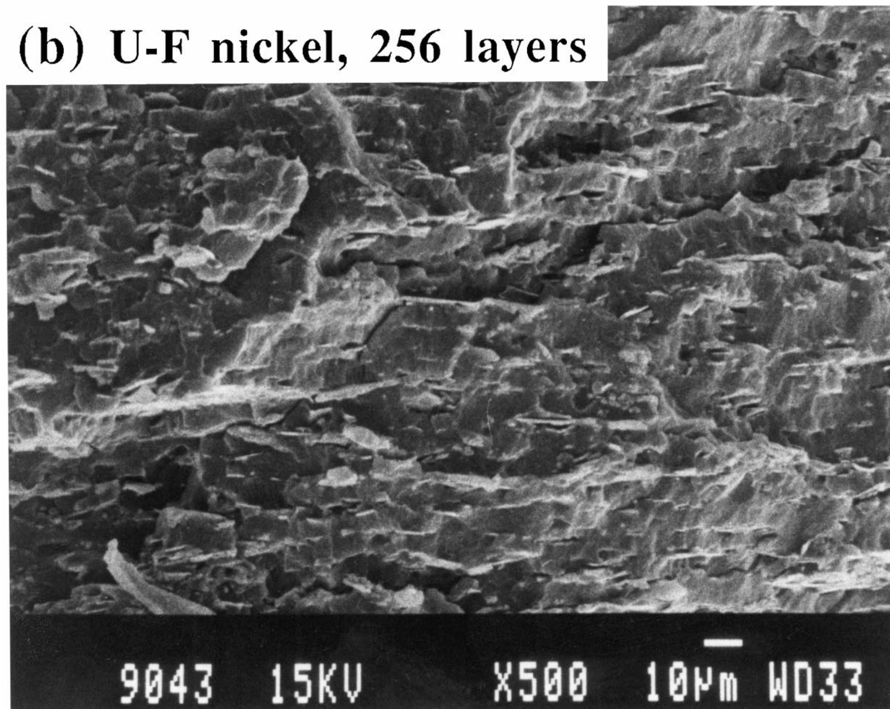


Figure 4 Scanning electron micrographs of U-F microlayers with thin layers: (a) Alternating 10% (v/v) copper-filled polypropylene and unfilled polypropylene with 128 layers; and (b) alternating 15% (v/v) nickel-filled polypropylene and unfilled polypropylene with 256 layers.

that particles of high aspect ratio can be rotated and aligned by even the moderate shear forces that arise as the melt spreads out in the press [20]. Therefore, some particle orientation was anticipated in the compression molded plaques.

Micrographs of copper-filled and nickel-filled F-F microlayers are shown in Fig. 2a and b. Geometric constraints imposed by layer multiplying produced very strong shear stresses which, in turn, caused remarkable particle orientation in the plane of the extruded layers. Compared to Fig. 1, particles were extremely well oriented in both nickel and copper systems.

Two examples of U-F microlayers with alternating filled and unfilled layers are displayed in Fig. 3a and b. The uniform alternating layers of filled and unfilled PP were clearly discernible and the particles in the filled layers were well-aligned in the plane of the layer. The average layer thickness in these microlayers was large compared to the particle thickness. The copper system had 16 layers with average layer thickness of 83 μm and the nickel system had 64 layers with average layer thickness of 15 μm. Because of the particle size difference, layer thicknesses were chosen so that the layer (H) to particle (h) thickness ratio, $K = H/h$, was comparable, i.e. $K = 28$ for the copper system with 16 layers, and $K = 15$ for the nickel system with 64 layers.

The U-F copper system with 128 layers ($H \approx 10\ \mu$m, $K \approx 3$) and the U-F nickel system with 256 layers

Figure 5 Voltage-current relationship of compression molded, metal-filled polypropylene: (a) 5% (v/v) copper; (b) 7.5% (v/v) copper; (c) 10% (v/v) nickel; and (d) 15% (v/v) nickel.

($H \approx 4\ \mu$m, $K \approx 4$) are depicted in the micrographs in Fig. 4a and b, respectively. In this case, where particle and layer thicknesses became comparable, only one or two particles fit in the thickness of the filled layers and the filled layers appeared as thin strips of well-aligned particles. The planar or two dimensional particle arrangement of U-F microlayers with a high number of layers was distinctly different from the three-dimensional particle structure in the U-F microlayers with fewer number of layers.

3.2. Electrical properties

3.2.1. Compression molded specimens

Fig. 5a–d exhibits typical voltage-current behavior of compression molded specimens with various copper or nickel content. The current was measured in the cross-plane direction. In all cases, non-linear voltage current behavior was observed when the voltage was applied for the first time. The non-linear effect was especially noticeable in systems with low conductivity. This behavior is shown in Fig. 5a and c for 5% copper and 10% nickel, respectively. Initially, when a small voltage was applied, the specimens had negligible conductivity. As the voltage increased, the behavior acquired the features

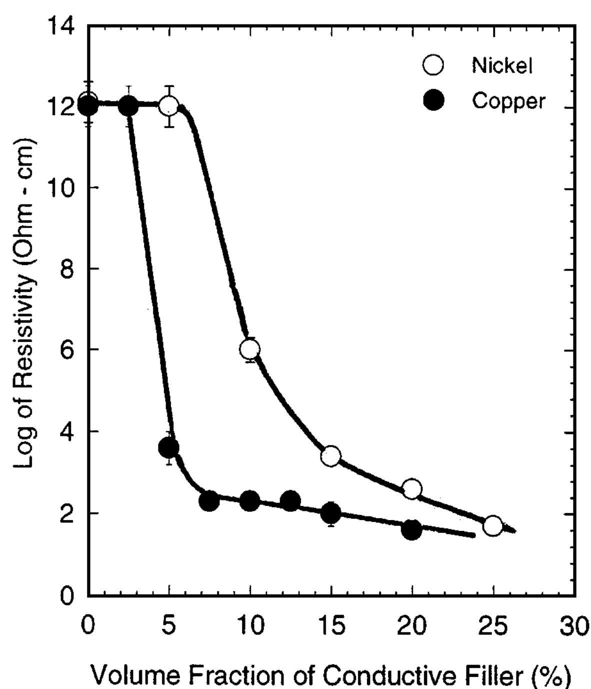


Figure 6 Logarithm of the volume resistivity versus filler volume fraction of compression molded copper-filled (solid circles) and nickel-filled (open circles) polypropylene.

of electrical break-down, i.e. the current changed very slowly with increasing applied voltage until the electric field strength reached a critical level at which the current increased dramatically indicating a significant drop in resistivity. The effect was less pronounced in the systems with higher initial conductivity as illustrated in Fig. 5b and d for 7.5% copper and 15% nickel. Regardless of the conductivity, the voltage-current characteristics during the second run were essentially linear in the voltage range studied. Third and succeeding runs were identical to the second run if the applied voltage did not cause a temperature raise in the specimen. The slope of the linear voltage-current relationship in the second and succeeding runs was used to determine the resistivity (R). Specific resistivity (ρ) was calculated from the sample contact area and thickness as $\rho = RA/L$ where A and L are contact area and thickness, respectively.

The effect of copper and nickel filler content on volume resistivity in the cross-plane direction of compression molded specimens is shown in Fig. 6. The resistivity of 15% nickel was also tested in-plane to determine any anisotropy in conductive properties caused by compression molding. The measurements revealed only slight anisotropy of conductive properties; the resistivity in-plane was about 4–5 times higher than cross-plane.

Compression molded specimens with low metal content were almost nonconductive. However, at a critical volume fraction, about 4% (v/v) for copper and 8% (v/v) for nickel, the resistivity fell sharply to 10^2–10^3 Ω cm which corresponded to the resistivity of a good semiconductor. Increasing the copper or nickel content further did not appreciably reduce the resistivity. Assuming that the critical volume fraction corresponded to a percolation threshold, a value of 4% for copper and 8% for nickel was significantly lower than 20–40% (v/v) for spherical particles. The higher specific surface area of platelet particles compared to spheres, which increased the probability of particle-particle contacts, could have accounted for the low percolation threshold. The lower value for copper, compared to nickel, probably should be attributed to its higher aspect ratio. An additional factor may have been the better intrinsic conductive properties of silver-coated copper flakes compared to nickel flakes. However, the similar resistivity of both systems with high particle content indicated that the aspect ratio difference was probably responsible for the lower percolation threshold of copper-filled polypropylene.

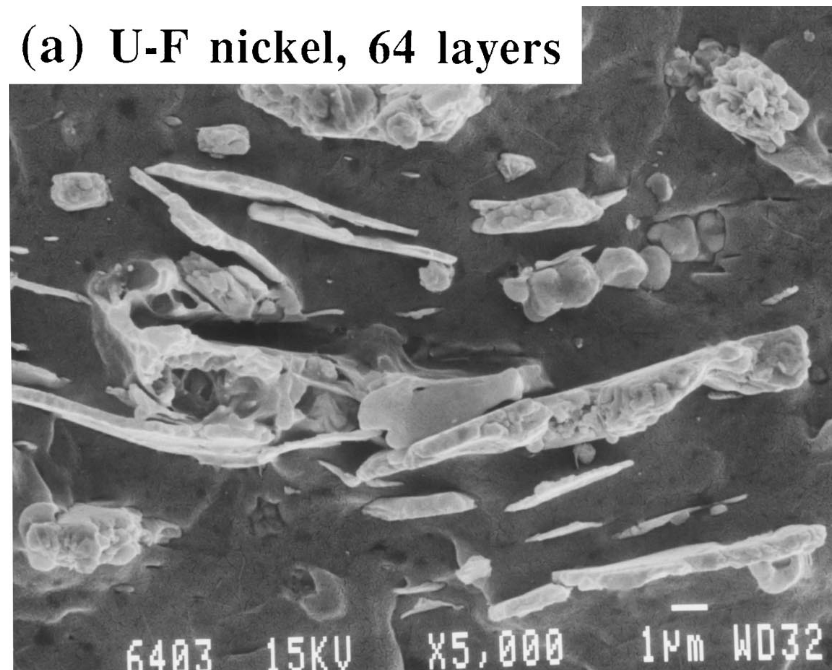
3.2.2. F-F microlayers

The resistivities of F-F microlayers measured in-plane and cross-plane are compared with the resistivities of the corresponding 10% copper-filled and 15% nickel-filled compression molded specimens in Table I. The table also includes the average layer thickness of microlayers calculated from the number of layers and the overall tape thickness. The F-F copper-filled microlayer exhibited about an order of magnitude anisotropy in the conductive properties. The cross-plane resistivity was comparable to the resistivity of the compression molded specimen and was higher than the in-plane resistivity. Particle orientation decreased the in-plane resistivity of F-F microlayers with 15% nickel by more than an order of magnitude compared to the compression molded specimen with the same composition. The cross-plane resistivity increased slightly. This produced about two orders of magnitude anisotropy in the conductive properties of the F-F nickel-filled microlayer. Compared to compression molding, where the particle orientation was not enough to produce more than slight anisotropy in the resistivity, microlayering was extremely effective for orienting the metal particles.

Typically, the analysis of conducting fillers in a dielectric matrix is based on assumptions of random particle distribution and orientation. However, the published results for an ordered array of isotropic elongated particles provide some insight into the behavior of aligned platelet particles [21]. From the prediction that the anisotropy reaches a maximum at the percolation threshold and rapidly declines thereafter, it is possible to understand why the copper-filled microlayer might have a lower anisotropy than the nickel-filled microlayer even though the particle aspect ratio is similar. From Fig. 6, it is evident that the F-F microlayer with 10% copper is well above the percolation threshold; therefore the anisotropy should not be large, and

TABLE I Resistivities of metal-filled microlayers and blend controls

Filler	System	Filler content % (v/v)	Number of layers	Layer thickness (μm)	K (Layer to particle thickness ratio)	Volume resistivity (Ω cm) $\times 10^2$	Direction
Ni	Blend	15	—	—	—	27 ± 12	Cross-plane
Ni	Blend	15	—	—	—	6 ± 4	In-plane
Ni	F-F	15	128	7	7	57 ± 11	Cross-plane
Ni	F-F	15	128	7	7	0.43 ± 0.11	In-plane
Ni	U-F	7.5	64	14	14	(120 ± 28)	In-plane
Ni	U-F	7.5	256	4	4	Non-conductive	In-plane
Cu	Blend	10	—	—	—	2 ± 1	Cross-plane
Cu	F-F	10	128	10	3	0.29 ± 0.05	In-plane
Cu	F-F	10	128	10	3	2.5 ± 1.2	Cross-plane
Cu	U-F	5	8	171	57	0.24 ± 0.01	In-plane
Cu	U-F	5	16	86	29	0.91 ± 0.14	In-plane
Cu	U-F	5	64	21	7	Non-conductive	In-plane
Cu	U-F	5	128	12	4	Non-conductive	In-plane



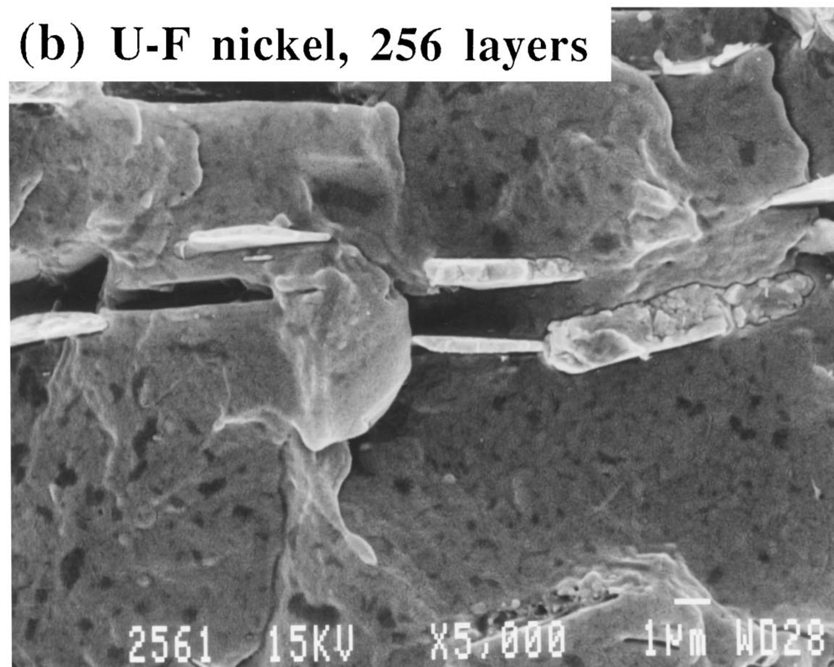


Figure 7 Scanning electron micrographs at higher magnification to show the particle orientation in the nickel-filled layers of U-F microlayers: (a) 64 layers; and (b) 256 layers.

furthermore the anisotropy can not be increased by increasing the filler loading. This is confirmed by the experiments. In contrast, the F-F microlayer with 15% nickel is within the transitional composition range. The maximum anisotropy that can be expected is equal to $(l/d)^2$ where l and d are particle length and thickness respectively. The observed anisotropy of the nickel-filled microlayer (two orders of magnitude) would require particles of aspect ratio 10, which closely coincides with the aspect ratio of these particles.

3.2.3. U-F microlayers

Anisotropy in the resistivity was practically ten orders of magnitude when layers of insulating polypropylene were alternated with nickel-filled or copper-filled layers in the U-F microlayers (Table I). The U-F nickel-filled microlayer with 64 alternating layers and a total nickel content of 7.5% by volume were conductive in the in-plane direction with the resistivity comparable to that of compression molded specimens above the percolation threshold, and displayed highly insulative properties in the cross-plane direction with a resistivity similar to that of unfilled polypropylene. In contrast, no in-plane conductivity was detected for the U-F nickel-filled microlayer with 256 layers. Copper-filled U-F microlayers with 8 and 16 layers and a total copper content of 5% by volume were also conductive in the in-plane direction with the resistivity comparable to that found in the in-plane direction for F-F copper-filled microlayers with 10% copper. However no conductivity was obtained

in U-F copper-filled microlayers with 64 and 128 layers. It appeared that the filled layers were conductive only if they were thick compared to the thickness of the flake particles. When the thickness of the filled layers approached the particle thickness, the conductive properties were lost.

This behavior can be understood by comparing the particle arrangement in thick and thin filled layers. Fig. 7a and b shows high magnification SEM micrographs of the filled layers of U-F nickel microlayers with 64 and 256 layers. Fig. 7a displays evidence of three-dimensional particle arrangement in the conductive U-F microlayer. In contrast, the filled layers of the non-conductive U-F microlayer in the Fig. 7b clearly resemble a two-dimensional particle layout.

Based on the micrographs, a model for the development of a conductive network in layers filled with oriented particles can be imagined as sketched in Fig. 8. For simplicity, the filled layer is considered as consisting of a number of imaginary sub-layers having a thickness equal to the particle thickness with uniform particles located in the sub-layers; the average particle volume fraction in the sub-layers is equal to the overall particle content in the filled layer. The conductive network results from geometrical contact of the particles. The network can result either from side-to-side contacts of particles located in the same sub-layer or from top-to-bottom contacts of particles located in adjacent sub-layers. Based on a volume fraction of 0.15 for nickel-filled layers and 0.10 for copper-filled layers, the probability of a side-to-side contact is much smaller than the probability of a top-to-bottom contact. Because most of the contacts can be viewed as occurring from top-to-bottom, not from side-to-side, the number of adjacent layers and consequently the layer thickness is a critical parameter for the development of a conductive network. With increasing number of layers, the layer thickness approaches the thickness of the sub-layer, i.e. the thickness of the particle. When this occurs, conductivity can be considered in terms of the two dimensional percolation of discs located in a plane. The theoretical value for the critical loading in this case increases to 0.45 [22, 23]. To achieve conductivity in microlayers with thin layers, the filler content would need to be significantly higher than the 0.15 and 0.10 required for thick nickel-filled and copper-filled layers, respectively.

The relationship of the transition to layer thickness is more appropriately described in terms of the number of oriented particles that can be accommodated in the thickness of a filled layer. The critical layer thickness required for conductive behavior would be thinner for thin particles and correspondingly thicker for thick particles with the same aspect ratio. Fig. 9 illustrates the transition from non-conductive to conductive behavior for both nickel and copper U-F microlayers with the resistivity plotted as a function of layer to particle thickness ratio (K). The data appear to superpose with a transition from two- to three-dimensional behavior at $K \approx 10$. It can be anticipated that the K value of this transition will depend on both filler volume fraction and particle aspect ratio.

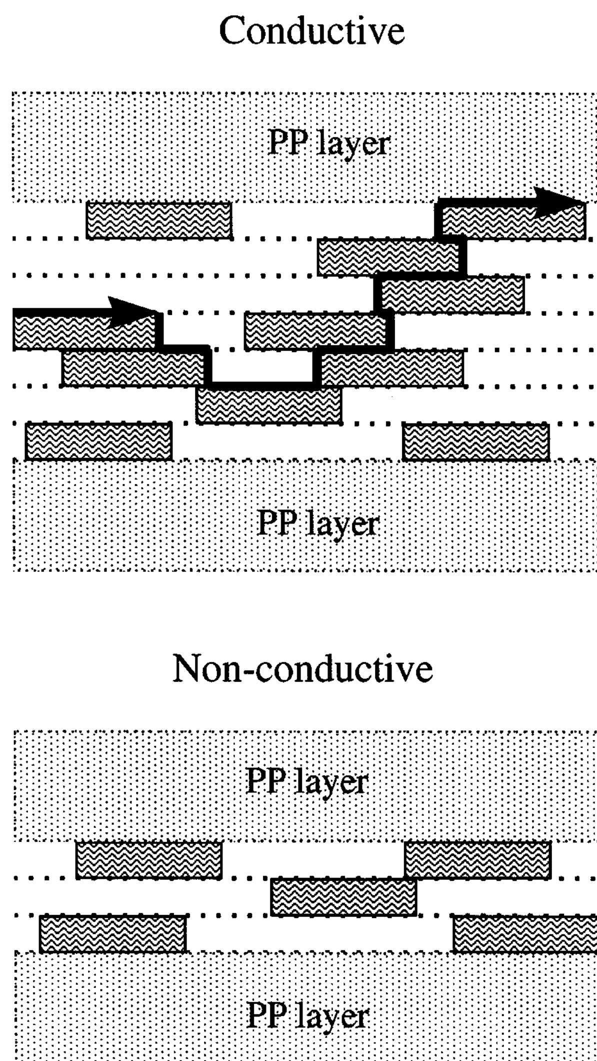


Figure 8 Sketch of the particle arrangement in thick and thin filled layers of U-F microlayers. The conductive pathway in the thick layer is indicated.

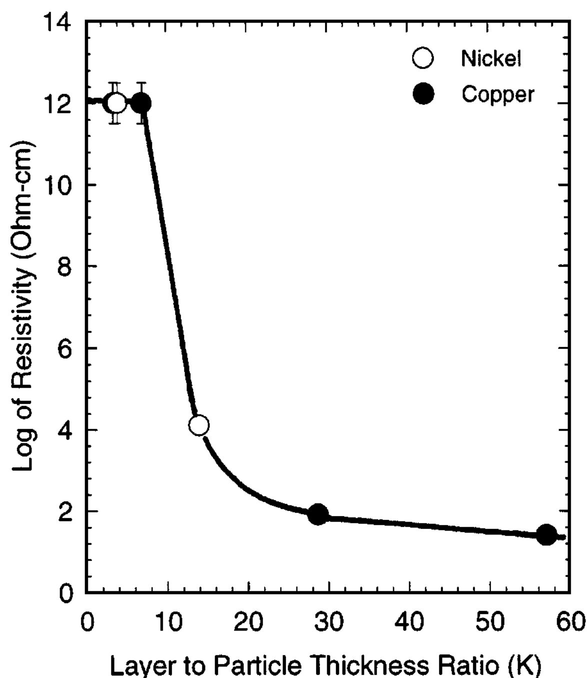


Figure 9 Logarithm of the volume resistivity versus layer-to-particle thickness ratio (K) for copper-filled (solid circles) and nickel-filled (open circles) U-F microlayers.

In summary, designed structures using microlayer coextrusion to manipulate orientation and distribution of metal flakes in a polymer matrix are demonstrated with copper- and nickel-filled polypropylene. The high degree of particle orientation achieved by microlayering is not possible with conventional thermoplastic processing methods such as extrusion or injection molding. The improved particle orientation is sufficient to increase the anisotropy in electrical resistivity by two orders of magnitude over compression molding. New possibilities for producing designed structures by microlayering arise when two components with different electrical properties are combined. This is illustrated with structures that consist of many alternating layers of a conducting polymer and a non-conducting polymer. Isolation of metal-filled layers by alternating them with unfilled layers results in materials with many independent conducting pathways. The versatility of microlayering makes it possible to examine transitional behavior when the layer thickness approaches the size scale of individual metal particles. In this case, the change from a three-dimensional particle array to a two-dimensional array produces a loss of conductivity in the metal-filled layers.

Acknowledgements
The authors thank Mr. Tony Ramic for assistance with the conductivity measurements. This work was generously supported by the Army Research Office (grant DAAG55-98-1-0311) and the National Science Foundation (grant DMR97-05696).

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Received 13 August and accepted 20 October 1998