Designing Polymeric Films Having Specific Metallic Luster

Ramesh M. Gohil

DuPont Co., Central Research and Development, Materials Science and Engineering Divison, Experimental Station, Wilmington, Delaware 19880-0323

Received 3 March 2011; accepted 27 August 2011
DOI 10.1002/app.35547
Published online 19 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The roles of blend composition and process parameters on the metallic luster of extruded polymer films and spray-coated samples have been investigated. The metallic luster is determined by the orientation of platy metallic particles which is determined from X-ray intensity ratio (XIR) of the (200) and (111) planes of the aluminum crystal lattice. The metallic luster is an optical property that is measured by the flop values derived from light scattering measurements. The XIR and flop are useful for monitoring the effect of changes in blend composition and process parameters. Addition of different shaped particles has a different effect on the orientation of aluminum flakes. It is shown that aluminum platy particles orient only when they are first dispersed in an appropriate dispersing polymer. A methodology is developed for matching the metallic luster of both spray-coated and extruded polymer resin formulations by coupling XIR data with the flop values. This methodology is shown to be useful for optimizing the process conditions and composition of polymeric blends containing aluminum flakes needed to achieve the required metallic appearance in polymer films and articles. J Appl Polym Sci 125: 327–338, 2012

Key words: polymer extrusion; WAXS; orientation; structure-property relations; polymer blends

INTRODUCTION

There are several automotive and nonauto applications where polymeric films and articles having metallic luster may be employed; e.g., painting and printing colors, trash containers, shoes, toys, beverage cans, snack packages, credit cards, indoor and outdoor ornaments, electromagnetic interference shielding, roof and tank coatings, solar cells, traffic signals, farm and garden coverings, plastic containers exhibiting high degree of barrier to atmospheric gases, films for filtering UV radiation to reduce polymer degradation, etc. In all the applications refractivity of the metallic looking objects is determined mainly by the orientation, distribution, size, and concentration of Al platelets, and the nature of additives and polymers.

Automobile paints having a metallic appearance are very popular. Silver luster paints made by blending aluminum (Al) platelets with polymer are extensively used in the auto industry. In the past, extensive studies have been carried out by the paint industry to find the parameters controlling the metallic luster and to develop methods for mimicking the metallic look.[1–6] Most of the studies are summarized in various patents and many details are not known. The metallic luster is adjusted by varying the characteristics of the Al particles and their orientation, composition, and process conditions. The metallic luster is quantified by measuring the percentage reflectance of light at different angles to determine the flop value.[1] It was shown that colorimeter L values give significant correlation when compared with the traditional visual methods of determining flake orientation.[4]

Many auto manufacturers are interested in producing lightweight polymeric autobodies, plastic films, and parts, which have a metallic appearance, thereby avoiding the conventionally used painting process.[6–15] The materials so produced can bypass the related environmental issues encountered by the coating industry.

Initially, the auto industry likes to manufacture molded parts such as car bumpers and trim. These can be fabricated by molding sheets of extruded polymers loaded with fillers. The base polymer is filled with aluminum flake to a composition of 5–15% by weight. The size distribution of Al flakes is such that the larger platy particles have a larger aspect ratio, i.e., the ratio of diameter to the thickness. The morphology resulting from the distribution of sizes of Al flakes and their orientation relative to the surface of a painted or molded article along with presence of fine particulate of inert filler material contribute to the

Correspondence to: R. M. Gohil (ramesh.m.gohil@usa.dupont.com).

Journal of Applied Polymer Science, Vol. 125, 327–338 (2012)

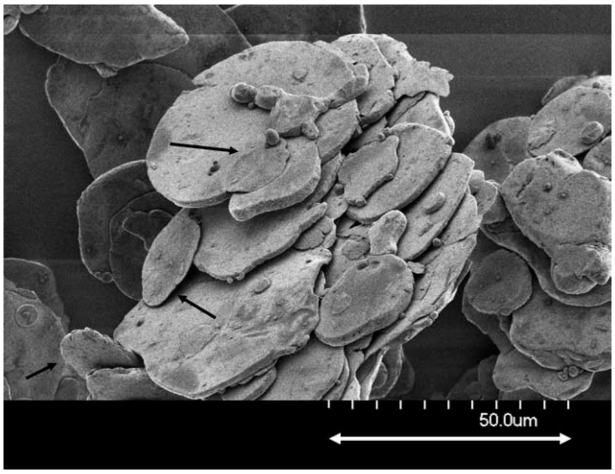

Figure 1 Scanning electron micrograph of aluminum platelets. Note that there are many particles with diameter less than 1.0 μm. Particles indicated by arrows have different orientation.

metallic appearance of the article. In most approaches, various types of polymeric materials were used, and the resulting 1000–1125 μm (40–45 mil) thick film consisted of several layers of coextruded materials. This configuration is thermoformed into various articles or auto parts.[7,10] The major challenge is to match the metallic appearance of body parts made by extrusion with spray-coated parts. The parameters influencing the metallic look are dependent on the type of process parameters, rheological characteristics of the formulation, sample thickness, characteristics of each component and their concentration in the formulation, etc. Thus, developing a process for extruding polymer parts that match the specific metallic luster of popular painted metallic auto finishes is very complex and challenging.

Our study is focused on (1) determining the major processing and formulation parameters that control the orientation of metallic platelets in spray-coated samples, (2) identifying the measureable properties which can assess any changes in process conditions and formulation, (3) developing a methodology for predicting the metallic luster for both the spray-coating process as well as the extrusion process for preparing articles made using Surlyn®, an ionomer of ethylene-*co*-methacrylic acid copolymer, and (4) show usefulness of the method for optimizing the composition of formulations and the process parameters to achieve a wide range of metallic appearances in polymeric films and articles.

EXPERIMENTAL

Source of materials

Al flake samples of different particle sizes were supplied by Silberline (Tamaqua, PA). As seen from the scanning electron micrograph (SEM; Fig. 1), the Al flakes used in this study are platelets. Note that there are very small platelets (less than 1.0 μm) on the surface of larger Al particles. The role of these small particles in the metallic look is not known. It is likely that such small particles can act as fillers or impurities and may influence the orientation of the platelets. This micrograph also shows the influence of large particles on the orientation of small platy particles (see arrows). The designations of the various sized Al flakes are; Silvet 220-20-E, 9.6 μm; Silvet 960-25-E, 14 μm; Silvet 890-30-E1, 19 μm; Silvet 860-30-E1, 24 μm; Silvet 790-20-E, 36 μm; Silvet 760-20-E, 54 μm. The Al particle sizes were determined using a SEM to analyze samples received from manufacturers. For this measurement, the Al flakes were dispersed in ethanol and spread on a carbon-coated SEM probe. The results were compared with the particle diameter, aspect ratio, and thickness data provided by the manufacturers.

A mica sample, Mearlin Sparkle 139P, average size of 24 μm, was received from Engelhard, Peekskill, NY. Glass flake samples were obtained from Glass Flake Limited, Leeds, England.

Samples of glass microspheres were obtained from Bangs Laboratories, Fisher, IN. Samples of glass spheres were obtained from Potters Industries, Carlstadt, NJ.

Surlyn SG771 NCB001, an ethylene-*co*-methacrylic acid copolymer neutralized with Na^+, will henceforth be referred to as an "ionic copolymer." Nucrel® is a random copolymer, ethylene-*co*-methacrylic acid, will henceforth be referred to as "EMMA copolymer." Both polymers were obtained from DuPont Packaging and Industrial Polymers, Wilmington, DE.

Methods of evaluating parameters

Metallic luster or look is defined as an optical property of metallic effect generated by metallic flakes. It varies with the viewing angle due to different degrees of orientation of metallic platy particles in coatings, plastic films, and articles. To define the metallic luster of spray-coated samples, the first task was to identify the measurable parameters that reflect the effect of changing a processing condition or the composition of the formulation. To characterize the metallic look we used two methods. One method is X-ray based and the other is the flop, which is based on measurement of optical properties.

X-ray intensity ratio

Al flakes are composed of platelets having an aspect ratio in the range of 10–28, and they can have a different orientation with respect to the substrate surface. The Al particle orientation influences the visual appearance of the sample surface after the spray

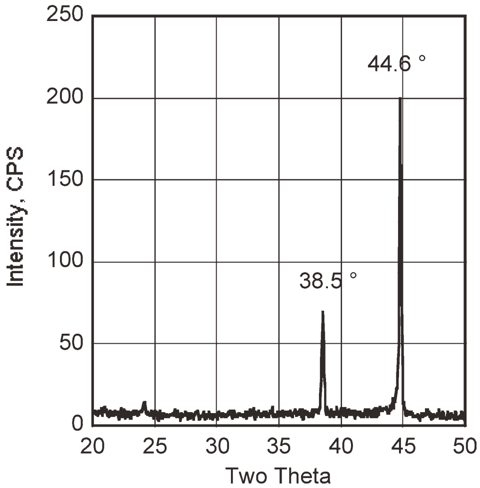

Figure 2 X-ray scan of aluminum flakes manifesting two peaks at 2θ values of 38.5° and 44.6° for the (111) and (200) planes, respectively.

coating process. The orientation of the Al platelets can be measured by wide-angle X-ray scattering (WAXS).

Aluminum has a cubic crystal lattice, type: Fm-3m (225), face centered cubic (FCC). In WAXS scan, two major reflections occur at 2θ of 38.5° and 44.6°, corresponding to the lattice planes of (111) and (200), respectively.[16] When the (200) plane of FCC is aligned in the plane of the wide surface of the Al platelets, then the (111) plane will be out of the plane. When Al platelet is aligned in the plane of the film substrate, the (200) plane is aligned in the plane of the film substrate. The measurement of the X-ray intensity (I) ratio (XIR) corresponding to the (200) and (111) crystal planes, I at $2\theta = 44.6°/I$ at $2\theta = 38.5°$, can provide information about changes in orientation of Al platelets with respect to the plane of the film surface.

WAXS was performed using a Philips 1/2 degree fixed slit diffractometer coupled to a Spellman high-frequency generator operating at 40 kV and 50 mA. The wavelength was 1.54 Å (copper anode). The scans were typically 20–50° 2θ, 0.02° steps with 2 s of data collection time between steps. The intensity is displayed in counts per second. Sample size was 3.5 × 5.0 cm.

Figure 2 shows a typical X-ray scan of Al flakes manifesting two major peaks corresponding to the (200) and (111) planes. There are no other major peaks in 2θ ranging from 20 to 50°.

XIR can be used to select the Al flake with the appropriate surface characteristics, to detect the orientation of Al platelets, and to determine the surface characteristics and distortion of Al platelets occurring during the processing step. Lower values of XIR indicate relatively highly random platelet orientation while a relatively high value indicates high orientation of Al platelets with respect to the film substrate. For a particular flake, the XIR value will depend on the conditions used to prepare the flake, and the orientation and concentration of the grains in the individual platelet. Each Al flake can have a different XIR value. Thus, our method will give the relative change in the orientation of the Al platelets in response to changes in process conditions and the composition of the formulation.

Flop index or value

Traditionally in the paint industry, the flop index or value (color shift) is a commonly known optical property of metallic pigments. It measures the ability of a metallic paint to appear to change colors and/or lightness and darkness depending on the angle from which a paint surface is viewed.[1,5]

The metallic effect perceived by the human eye when looking at films containing metallic flake is a combination of directional reflection of the incident light from the metallic flake surface and light scattering at the edges and unevenness on the surface of the Al platelets.[1] Absorption of light by the binder polymer also influences the reflection of light, as do the Al particle size distribution and aspect ratio. So orientation of Al platelets in the film is not the only factor governing the metallic look of a particular sample. Coarse metallic particles with average particle size of 25 μm or larger can induce a sparkling effect. XIR differs from flop as it does not take into account the absorption of a polymer, edge effect, and only measures the orientation of the (200) lattice planes with respect to the plane of the particle surface.

Flop is calculated from the intensities of visible light scattered when measured from three different angles (Fig. 3). Visible white light is incident on the surface at 45°. A multiangle spectrophotometer such as an X-Rite TM Model MA68 multiangle spectrophotometer is used to measure the amount of reflectance (L) of a source lamp at various viewing angles (Fig. 3). The light reflected intensity is measured at different angles; 15° from specular (near spec, L_{ns}), 45° (flat, L_f), and 110° (high, L_h). Flop provides real visual effect by using daylight that consists of a large range of wavelengths. The flop value is calculated using the equation below,[1,5]

$$\text{Flop} = 2.69(L_{ns} - L_h)^\wedge 1.11/L_f\ ^\wedge 0.86$$

Low flop value indicates a low degree of variation of light intensity with changing viewing angles.

Extrusion of films

In the first step of the film manufacturing process, platy additives (Al and mica) are dispersed in

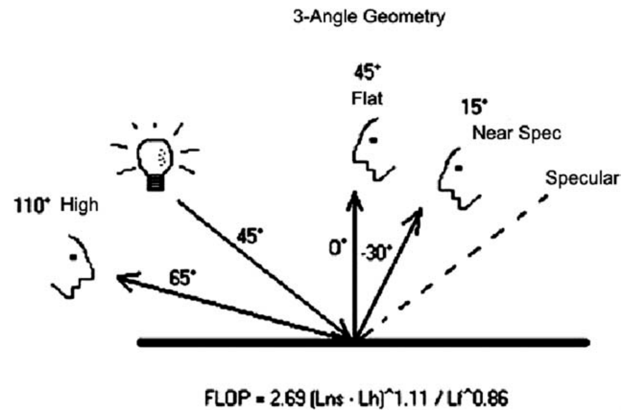

Figure 3 Intensity is measured at three different angles to calculate the flop index, an optical property of the sample composed of aluminum particles.

EMMA copolymer, which aids in dispersing various additives in the ionic copolymer. To make a master batch, additives are dispersed in EMMA copolymer by dry blending and then melt blended in an extruder.

Films of ionic copolymers and their blends were made on a 28-mm (Model ZDSK-28 II) and 30-mm twin screw extruder (Model ZSK-30), Werner and Pfleiderer, Stuttgart, Germany. We used screw type: MGW # 3, having a severity index of 214. For these extruders, the maximum torque is 9 Nm. The torque value of these extruders is expressed as % which is calculated considering the maximum torque of 9 Nm.

About 40–45 mil (1000–1150 μm) thick samples were coextruded on a multilayer extrusion line. In the coextruded samples, the thickness of each layer was varied. The first layer was 5 mils of Surlyn, ionic copolymer. The second layer containing Al particles in ionic copolymer was 10–12 (250–300 μm) mils thick. The third layer containing reground ionic copolymer was 15 mils thick. The fourth layer of ethylene propylene rubber was 15 mil thick. This configuration was then thermoformed into an article or auto bumper. The important extrusion parameters used for making Surlyn films are compiled in Table I.

RESULTS AND DISCUSSION

As indicated in the introduction, our intention was to make extruded metallic-looking plastic autobody parts whose appearance matches the look of the existing spray-coated autobody reference sample.

In Part-1, we discuss the key spray-coating process and formulation parameters that have a discernable effect on the values of XIR and flop. We then utilize those parameters to establish a relation between XIR and flop values. Then we explore the usefulness of that relation for predicting the metallic appearance.

In Part-2, we use the information gained in Part-1 to establish a methodology for achieving a specific metallic look in extruded polymeric films or parts. This involves pairing the XIR value with the flop value to match the metallic appearance of a spray-coated sample.

Studies on spray-coated samples

Experimental variables

Parameters controlling metallic looks can be divided in two groups: (a) Al flake characteristics: surface shape or roughness, aspect ratios, thickness and distribution of platy particles, surface treatment, spatial orientation of crystalline grains in platelets, concentration of pigments, and the presence of other fine additives, etc., and (b) the process variables for spray coating: gun pressure measured in psi, spray distance, solvent used, nature of polymer or binder used, room temperature, humidity, coating thickness, viscosity, paint flow rates, etc. These parameters influence both orientation of Al platelets and metallic looks of the sample surface.

Effect of Al platelet and process parameters on flop and XIR

Samples were spray coated with a formulation containing 6-wt % Al flake using a gun pressure of 60 psi and a spray distance of 10.5″. As seen from Figure 4, increasing Al particle size leads to a decrease in XIR values. Large particles of Al show lower values of XIR. It indicates that the randomness of the Al platelets has increased as the particle size has increased. This may be due to the failure of larger Al platelets to stack uniformly in the plane of the substrate. Smaller particles show relatively high XIR values which indicate a relatively more consistent platelet orientation with respect to the film surface.

TABLE I
Effect of Extrusion Parameters (30-mm twin screw extruder) on the XIR and Flop Values of Surlyn® Containing 8% of 36-μm Aluminum Flake (Silvet 790-20E)

ID	Screw speed (RPM)	Rate (PPH)	Melt temp. (°C)	Torque, % (Nm)	Pressure (psi)	XIR, I45/I38.5	Flop
1	100	28	217	91 (8.19)	210	1.996	12.5
2	200	22	212	70 (6.3)	150	1.90	11.7
3	300	22	232	78 (7.02)	200	1.89	11.5
4	200	22	216	65 (5.85)	170	1.85	11.8
5	100	26	223	100 (9.0)	200	1.80	12.2
6	200	20	227	75 (6.75)	170	1.79	11.6
7	300	20	229	72 (6.48)	170	1.78	11.5

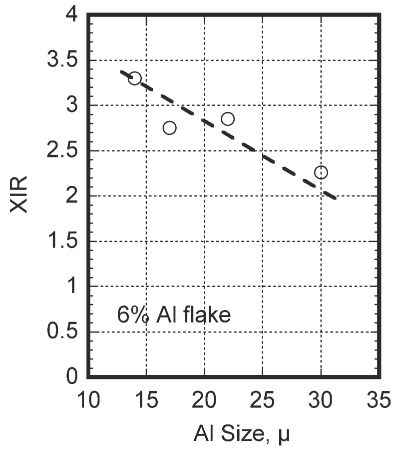

Figure 4 Variation of XIR values with aluminum particle size.

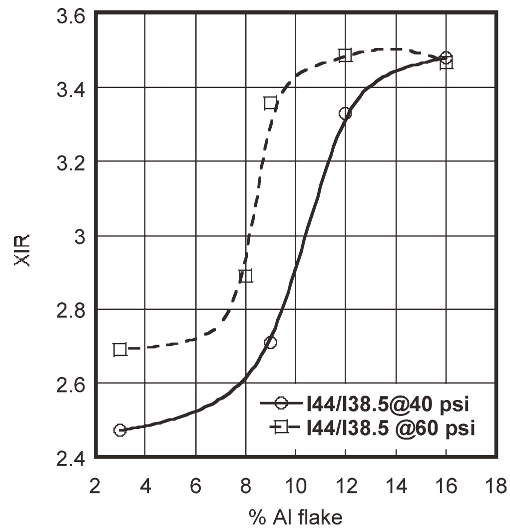

Figure 6 Variability of XIR with aluminum flake concentration at two different gun pressures.

As seen in Figure 5, flop values, which denote the optical properties of the surface, increase as the Al particle size increases. To achieve a high flop value, it is necessary to use larger particle size Al flake. It can also be concluded that a bimodal distribution of Al particles is not preferred to achieve the high flop value. A low flop value seen in a sample containing small Al particles (Fig. 5) having relatively high orientation may be due to the contribution of particle "edge effect," particle surface morphology, and the presence of very small particles on the surface of larger Al platelets (Fig. 1).

Figure 6 shows the effect of Al flake (Avg. size = 15 μm) concentration on XIR values at different gun pressures. XIR value depends on the concentration of Al flake and changes rapidly at concentrations of 8–12%. Depending on the gun pressure, XIR values can range between 2.7 and 3.3 at 9% Al flake concentration. XIR at low gun pressure is always low up to Al flake concentration of 14%. It indicates that at high gun pressure the Al platelets are aligned with the wide plane of the film substrate. High alignment of platelet orientation occurs at 9–11% Al flake concentration. To achieve an XIR value of 3.3, a lower concentration of Al particles is required at high gun pressure. XIR values level off at higher Al particle concentration (12%) and thereafter gun pressure has no effect.

The relation between flop values with Al concentration is complex (Fig. 7) but it indicates that at a particular gun pressure the flop value decreases with the concentration of Al flake. As seen from Figure 7, at 60 psi gun pressure flop remains unchanged up to 8 wt % Al concentration and then decreases abruptly as the concentration of Al particles increases.

Figure 8 shows the relationship between flop and XIR values at different gun pressures and Al flake

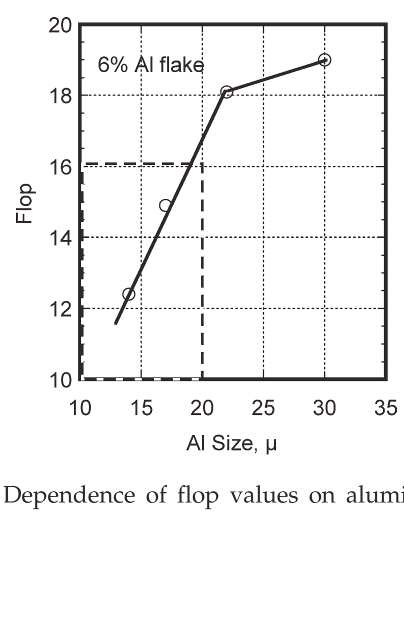

Figure 5 Dependence of flop values on aluminum particle size.

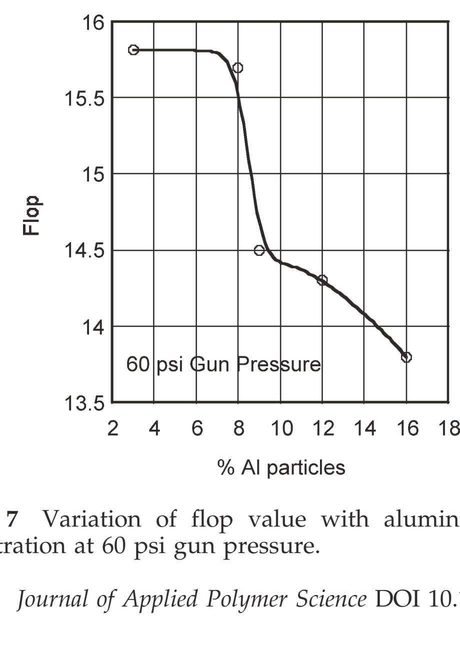

Figure 7 Variation of flop value with aluminum flake concentration at 60 psi gun pressure.

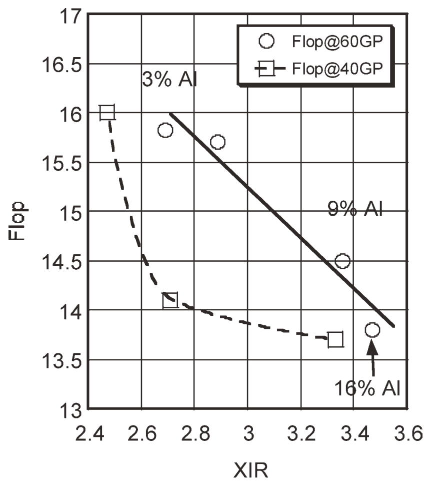

Figure 8 Relationship between XIR and flop values at different gun pressures and aluminum flake concentrations.

concentrations. At higher gun pressure, flop values decrease linearly with the increasing Al flake concentration. This is not the case at lower gun pressure. The effect becomes pronounced at low Al flake concentrations and a gun pressure of 40 psi. At low Al particle concentration, the flop value is dependent on the gun pressure.

These results show that any changes in the process conditions that influence the platelet orientation can be monitored by XIR and flop. These parameters can provide a method for fine-tuning the process conditions. It seems that coupling the XIR with the flop measurements can help us to select the gun pressure, and Al particle concentration needed to adjust flop and XIR to achieve a desired metallic look.

Spray-coated reference sample

Our spray-coated commercial reference sample is designated as Ref-AY-111. Characterization of the size, shape, and distribution of Al particles of the reference sample was carried out using reflection microscopy. The average particle size (14 μm) was determined from a reflection micrograph by a computer-aided program [Fig. 9(a)]. The white lines seen on the particles are drawn by computer to calculate the average particle size. To determine the distortion of particles these particles were then compared with the morphology of the as received Al flake.

The X-ray scan of the reference sample Ref-AY-111 [Fig. 9(b)] shows that the XIR is 3.3 and the flop is 12.5. It also shows extra peaks which correspond to mica. The peak locations can be compared with the X-ray scan of a mica sample [Fig. 9(c)] which was prepared by dry blending mica with EMMA copolymer and then extruded into pellets. These pellets were then compression molded into films. The peaks corresponding to Al (Fig. 2) do not superimpose with the mica peaks [Fig. 9(c)].

In addition to the orientation of Al particles, X-ray study is also useful for detecting the presence of mica in unknown reference samples. For further comparison, the X-ray scan of an ionic copolymer sample containing 10% of 9.5 μm Al particles and 1% mica is shown in Figure 9(d).

Relation between XIR and flop

Figure 10 summarizes the flop and XIR values of commercial painted samples along with our spray coated reference sample Ref-AY-111. XIR values increase with increasing Al flake concentration or reduction in the Al flake size. Higher orientation of Al particles occurs as particle size decreases. Larger Al particles give higher flop values and increase the sparkling effect. It was already noted that higher flop values provide a bright visual effect.[6] It seems that to achieve a more appealing silver metallic appearance the XIR and flop values for our sample should lie in the fourth quadrant of Figure 10.

Figure 10 shows that the XIR values for the painted samples exceed a value of 1.5, more preferably 2.0. Thus, the metallic appearance of many popular autopaints falls into the second and fourth quadrants. The metallic look of our reference sample is also in the fourth quadrant.

In our initial experiment with extruded films of ionic copolymer, we never reached a XIR value of 2.0, and our values lie mainly in the third quadrant. This result indicated that we needed to find a way to raise the XIR value to match the values of the spray-painted reference sample Ref-AY-111.

Extrusion of polymer films

Effect of the extrusion parameters on XIR and flop

The process parameters, which can affect the orientation of Al particles and thereby the metallic look, are die gap, extrusion temperature, pressure, melt rheology, polymer throughput, screw speed and type, and the nature of additives such as mica, TiO_2, UV stabilizer, slip additive, film thickness, and tension applied during casting film on the casting roll. The degree of particle dispersion and particle distortion are important factors for samples made by extruding polymer blends that contain platy particles. Also, impurities in the polymer, additives, thermal stabilizers, etc., can have an influence on absorption of light. Melt rheology can also influence the metallic look. Thus, to match the metallic look of painted parts with extruded parts is a multiphase undertaking.

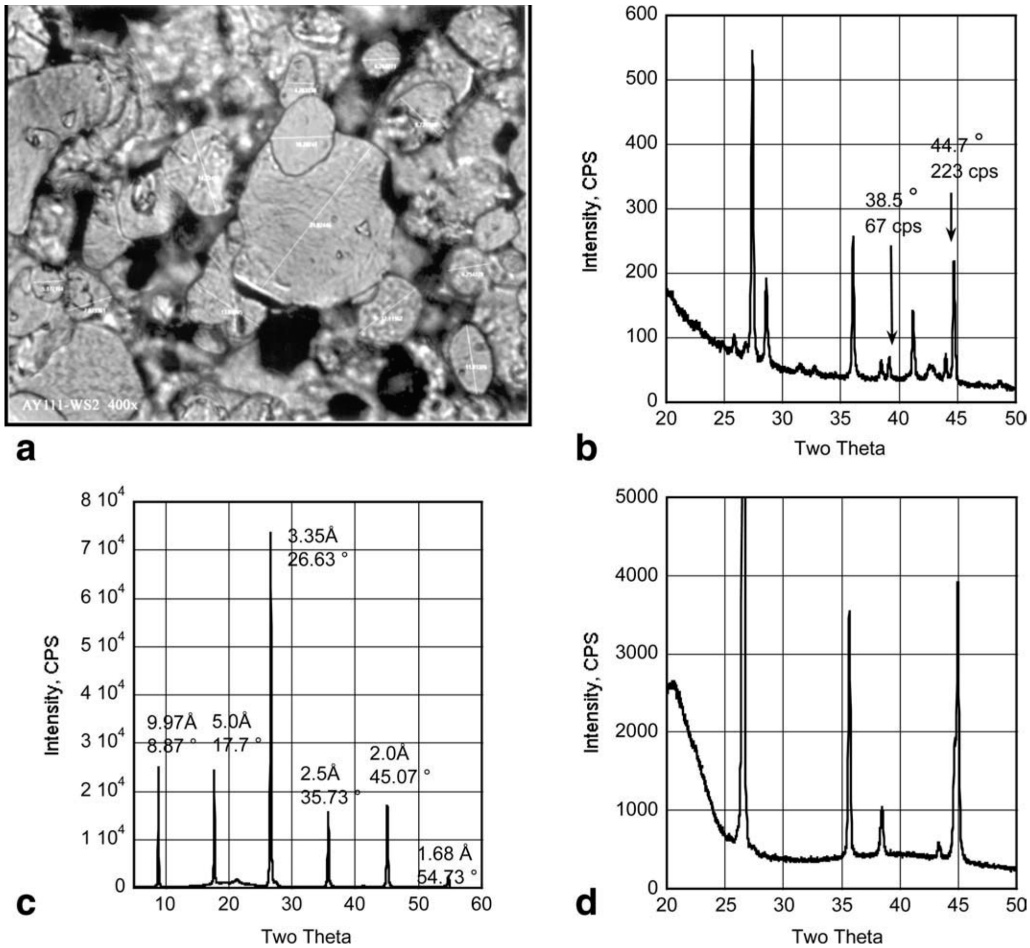

Figure 9 (a). Reflection micrograph of spray-coated reference sample (AY-111) showing variation in particle size. (b) X-ray scan of reference sample (AY-111) containing aluminum and mica flake. XIR value is 3.3. (c) X-ray scan of only mica flake blended with Nucrel® polymer. (d) X-ray scan of Surlyn® film containing 10% of 9.5-μm aluminum particles and 1% mica flake.

Silvet-790-20-E aluminum flake (36 μm average diameter) was used at 8% concentration in an ionic copolymer. The results are shown in Table I. Samples 5, 6, and 7 were fed using the side feeder on a twin 30 mm extruder. There was no appreciable variation in XIR values with feed rate of polymer, (pounds per hour, PPH) from 20 to 28, torque from 70 to 100% (6.3–9.0 Nm) and melt temperature from 212 to 232°C. In all the cases, the XIR values (1.8–2.0) were within experimental error.

From the separate experiments, we found that at melt temperatures above 200°C, variation in the screw speed from 100 to 300 RPM does not influence XIR and flop values. As seen in Table I, following an increase in PPH from 22 to 28, the XIR and flop vary by less than 7%. From our polypropylene-based formulation, an increase in melt temperature from 180 to 200°C can cause a 12% increase in the values of XIR and flop (Gohil, unpublished work). Thus, torque and pressure values are dependent on the rheology of the polymer blend-containing Al flake which is determined by the extrusion temperature as well as the nature of the particles and their concentration and distortion during extrusion processing of blends. Thus, the orientation of Al particles (XIR) is dependent on the rheology of the blend, which can influence the metallic look.

In conclusion, the variation range in the film extrusion conditions (screw speed, pounds per hour (PPH), melt temperature, and torque) we selected for ionic copolymer blends do not appreciably influence the Al particle orientation (Table I) or XIR and flop values.

Effect of Al particle sizes and concentration

In our study, a master batch of Al platelets was made in EMMA copolymer. The concentration of Al particles in master batches varied from 30 to 80%. These master batches were blended with an ionic copolymer to achieve the desired Al concentration. Films were coextruded as mentioned in the Experimental section.

The effect of Al particle size on XIR and flop values of spray coated and coextruded samples is

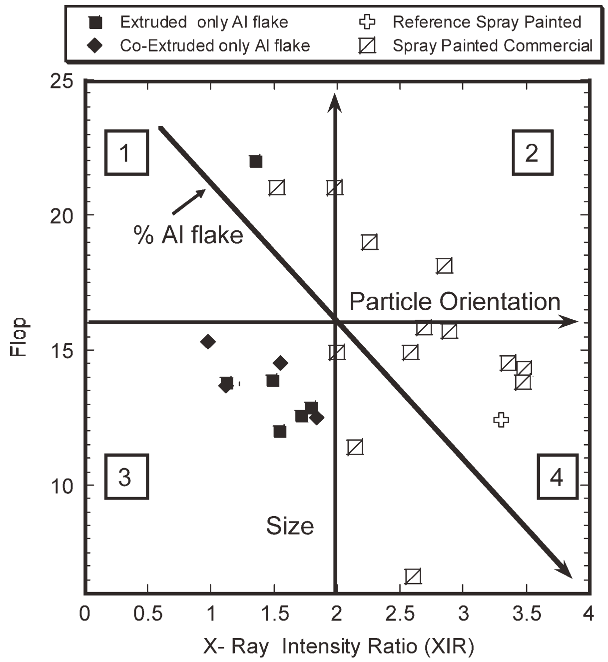

Figure 10 Summary of XIR and flop values for commercial spray-painted samples and coextruded polymer samples containing aluminum flake. Numbers 1–4 indicate the particular quadrant of the graph.

shown in Figures 11 and 12, respectively. The concentration of Al platelets in ionic copolymer film is 6%. In spray-coated samples, XIR decreases with increasing Al particle size. Low XIR indicates a more random Al particle orientation. The XIR values of extruded polymer samples do not increase appreciably even when using Al particles of different sizes.

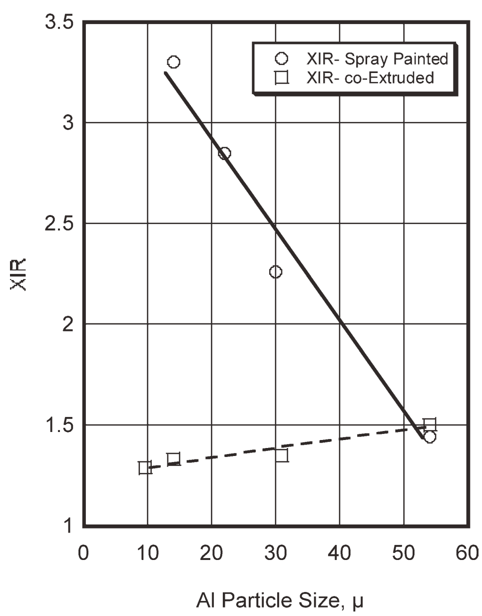

Figure 11 Comparison of effect of aluminum particle size on XIR values of spray-painted and coextruded Surlyn® samples.

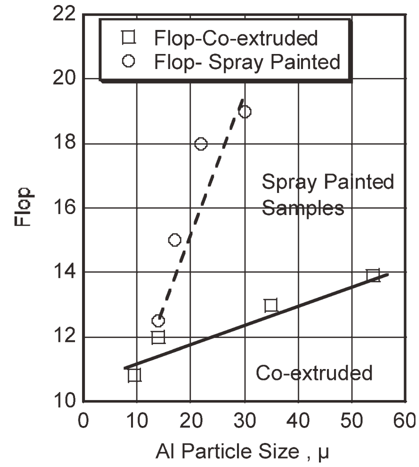

Figure 12 Comparison of effect of aluminum particle size on flop values of spray-painted and coextruded Surlyn® samples.

The results show that for a particular particle size XIR value is method dependent.

Figure 12 shows that in spray-coated samples, the flop value increases rapidly as particle size increases. In coextruded samples, flop slowly increases with the Al particle size while XIR values are less than 2.

To evaluate the effect of Al particle concentration on XIR and flop values in ionic copolymer films, Al flakes of 9.5–36 μm have been selected. To make a desired concentration in ionic copolymer, we have used master batches having different concentrations of Al flake (9.5 and 14 μm). The Al concentration in master batch does not affect XIR values. As seen from Figure 13, even when changing Al concentration it is not possible to increase XIR values above 1.8.

In extruded films of ionic copolymer-containing Al platelets, flop values remained unaffected by varying the concentration of Al particles but are a

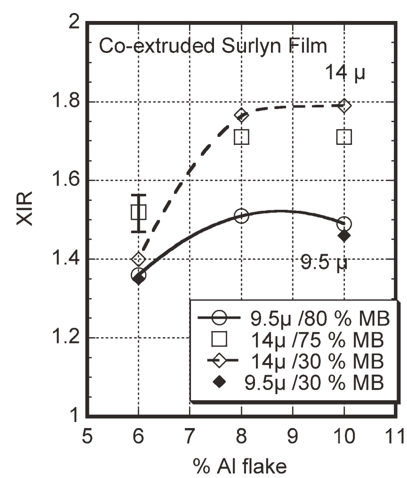

Figure 13 XIR dependency on concentration of aluminum flake and masterbatch compositions.

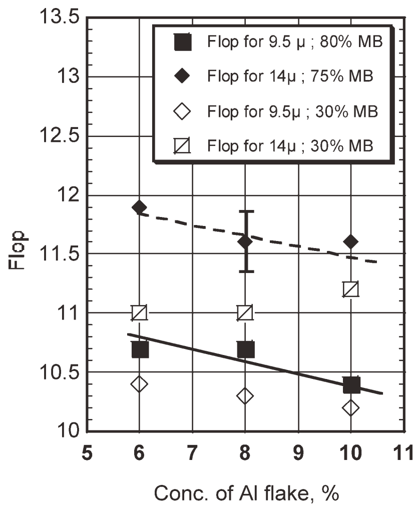

Figure 14 Flop-value dependency on concentration of aluminum flake and masterbatch compositions.

function of particle size (Fig. 14). It is observed that the master batches containing higher percentages of Al flake of a particular size give slightly higher flop values for 14 μm Al flake (see error bars).

In this section, we have seen the effect of Al particle size and concentration, and Al flake concentration in master batches on flop and XIR. It is realized that all the above variables cannot lead to XIR values similar to the reference sample, Ref-AY-111. From Table I and Figures 11 and 12, it is apparent that the processing conditions for extruded samples cannot lead to higher Al platelet orientation with respect to the surface of the film. Hence, both methods lead to different Al particle orientation and thereby different metallic looks.

Therefore, in the next section, we have explored methods to enhance the XIR value by adding mica or glass flake to blend formulations.

Effect of mica and glass flake

XIR values of the extruded films containing Al particles of 9.5–35 μm are less than 2.0 (Figs. 10, 11, and 13; Table I). We evaluated the effect of % mica (average size 24 μm) on XIR and flop values when used with Al flakes having particle sizes ranging from 9.5 to 35 μm. In our study, we used mica concentrations of 0–4% while the concentration of Al flakes varied from 6 to 10 wt %. As seen in Figure 15, mica flake has greater influence on XIR when Al platelets have sizes in the range of 9.5–14 μm. Mica has no effect on XIR values if the Al particle size exceeds 24 μm. There is no variation in XIR for 24- and 35-μm Al flake. XIR values between 2 and 4 can be achieved by incorporating mica with 9–20 μm Al flakes (Fig. 15). The required percentage of mica is less than 2.0 if Al particle size is between 9.5 and 14 μm. Thus, mica particles aid in aligning Al particles during the extrusion process. In summary, our study guides us to select the correct Al particle size and mica concentration to adjust the goal value of XIR.

In samples containing 9.5 μm Al flake, blending with virgin mica (mica not dispersed in EMMA copolymer) does not change XIR values (Fig. 15). However, when mica is dispersed in EMMA copolymer before blending with Al flake, a remarkable increase in XIR values is observed. Therefore, it is important to disperse Al flakes in appropriate polymer matrix before blending in ionic copolymer. So, our method can be used to determine the appropriate polymer for dispersing Al particles or indicate that a particular polymer is not acting as a good dispersing agent.

As seen in Figure 16, addition of up to 4% mica to Al flakes of 14 μm or smaller showed no effect on the flop value. But the flop is dependent on Al particle size. Addition of 1% mica to a preparation made with larger Al flake (34 μm) causes an initial reduction in flop value, but no further reduction in flop is seen as more mica is added. Despite the reduction of available Al particle surface, (the mica flake covers the Al particles) flop does not change as more mica is added. This indicates that the light-reflecting characteristics of both the mica and Al particles are similar. Therefore, the required flop value can be a decisive factor when choosing the size of Al particle along with a particular mica flake concentration. Our study points to a procedure to select the appropriate Al particle size to achieve a required flop value.

Mica is a platy particle so to see if any other platy particles can have an effect on XIR and flop values

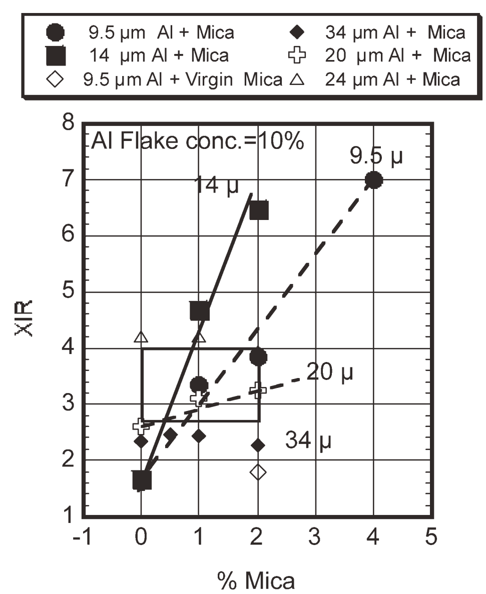

Figure 15 Effect of mica (24 μm) concentration on XIR values for Surlyn® containing different aluminum particle sizes. Aluminum flake concentration in Surlyn® is 10%.

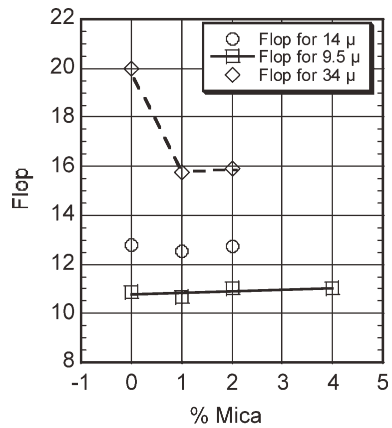

Figure 16 Effect of mica flake concentration on flop values for Surlyn® containing different aluminum particle sizes. Aluminum flake concentration in Surlyn® is 10%.

like that seen in Figures 15 and 16. We selected platy glass flake (50 μm mean size) as a substitute for mica. We extruded two sets of sample films as described below.

In Set-I, a master batch of 20% glass flake was blended with EMMA copolymer. A 10% concentration of 17 μm Al flake in ionic copolymer was kept constant in all samples, while the concentration of glass flake was varied between 0.5 and 2%. The resulting XIR-1 and flop-1 values are compiled in Table II. Note that as the concentration of glass flake increases, XIR values also increase while the flop values remain the same within experimental error. This trend is similar to that noted when mica was blended with ionic copolymer containing Al flake.

In Set-II, the glass flake was used as received (not dispersed in EMMA copolymer in the same concentrations as Set I). Here, the glass flake had no appreciable effect on XIR-2 and flop-2 values (Table II, Set-II). These results are also consistent with those observed with the virgin mica used previously (Fig. 15). Therefore, it becomes clear that any chosen platy additive should be first dispersed in an appropriate low melting polymer matrix like EMMA copolymer. This procedure ensures a uniform dispersion of the platy particles and may prevent any distortion to the platy particles.

TABLE II
Effect of Glass Flake (20% glass flake melt blended with Nucrel® polymer) on XIR and Flop Values

		Set-I		Set-II	
ID	Sample details	XIR-1	Flop-1	XIR-2	Flop-2
36-6	17μm 10% Al	1.66	12.53	1.87	12.47
36-7	17μm 10% Al/0.5% glass flake	1.74	12.17	1.92	12.5
36-9	17μm 10% Al/2% glass flake	2.5	12.5	1.85	12.14

Effect of spherical particles

A constant 10 wt % concentration of 24 μm Al flake (Silvet 860-30-E1) was blended in ionic copolymer and the concentration of spherical TiO_2 particles was varied between 0.2 and 1%. Variation in XIR and flop values with the addition of TiO_2 is shown in Figure 17.

Results show that addition of less than 0.2 wt % TiO_2 decreased the XIR value from 4.2 to 3.4 and then further addition of TiO_2 does not appreciably decrease the XIR values. This indicates that addition of a small amount of TiO_2 particles change the orientation of Al particles from higher orientation to a relatively more random orientation. With increasing TiO_2 concentration, the flop value continuously decreases. TiO_2 particles influence light scattering. The effect of the interaction of visible light with TiO_2 particles on flop values requires further investigation.

From Table III, it is also seen that glass spheres have an effect on XIR and flop values similar to that shown by TiO_2 particles. Flynn and Truog mentioned that addition of microspheres to paint enhances the randomness in flake orientation,[6,17] which is also seen in our extruded film. Increase in randomness in orientation of Al platelets decreases the flop values. To match the desired look of spray coated samples using extruded polymer films, the values of flop and XIR in extruded samples could be adjusted using the platy and spherical particles.

This particular Al flake sample (Fig. 17) showed a relatively higher value of XIR than the other samples we investigated. Such a change in XIR can result from a difference in particle size distribution, surface characteristics of particles, processing condition of Al particles, presence of impurity or other additives,

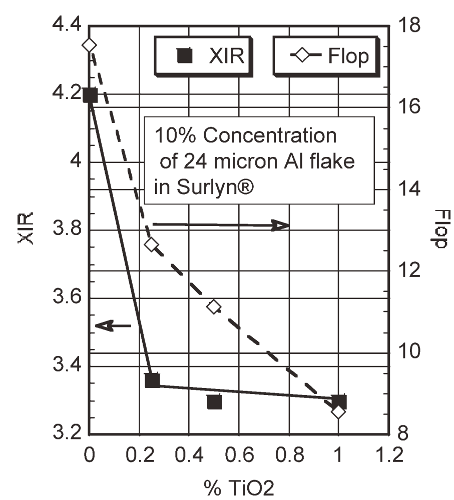

Figure 17 Effect of TiO_2 concentration on the XIR and flop values of Surlyn® film containing 10% of 24 μm aluminum flake.

TABLE III
Effect of Spherical Particles (TiO_2 and glass spheres) on XIR and Flop Values of Surlyn® Containing 24-μm Aluminum Flake (Slivet 860-30-E1)

ID	Composition of surlyn; Al size/(% of flake)/% TiO2 or glass sphere/(size)	XIR	Flop
109-7	24μm/(10%)	4.24	17.53
129-2	24μm/(10%)/0.25% TiO2/(0.3μm)	3.36	12.66
118-2	24μm/(10%)/0.5% TiO2/(0.3μm)	3.30	11.14
118-3	24μm/(10%)/1.0% TiO2/(0.3μm)	3.30	8.56
13-7	24μm/(10%)/0.5% glass sphere/(3μm)	3.22	12.97
13-8	24μm/(10%)/1% glass sphere/(3μm)	2.74	11.76
13-9	24μm/(10%)/0.2% glass sphere/(0.3μm)	3.60	14.84
13-10	24μm/(10%)/0.5% glass sphere/(0.3μm)	3.45	14.10

and the nature of the carrier used to supply Al flakes. The variation in concentration of very small flake particles on the surface of larger flakes (Fig. 1) in the sample prepared in various manufacturing conditions could be similar to spherical particles.

Mapping the metallic appearance

The flop and XIR values for ionic copolymer films extruded using a variety of conditions for the size and concentration of Al flake, mica, and TiO_2 are shown in Figure 18. XIR and flop values for all the extruded samples without mica lie in the third quadrant (XIR less than 2.5) as shown in Figure 10. Addition of mica in formulations of ionic polymer allows us to enter into the fourth quadrant. The metallic appearance of many popular auto paints fall into the second and fourth quadrants. Our goal was to make polymer films which can match a spray painted commercial reference sample (Ref-AY-111). The XIR and flop values of the reference sample are shown in Figure 18. Visual inspection of the extruded samples having XIR and flop values similar to our reference samples showed similar metallic appearance. Despite the process differences, it is possible to match XIR and flop values similar to a reference sample.

SUMMARY

We have conducted a structure-property–processing study on spray-coated samples and extruded polymeric films to achieve a specific metallic look. The samples were made by varying the compositions of the formulations, the nature of Al flake, and process conditions. We found that the parameters XIR and flop are very sensitive to changes in process conditions and the characteristics and the concentration of Al flakes in a master batch. Therefore, the study was undertaken with the underlying hope to use the findings to explore usefulness of XIR and Flop for matching the metallic look of extruded polymeric parts and films.

In the spray-coating process, XIR values increase with increasing Al particle concentration but decrease with increasing Al particle size. During the spray-coating process, XIR is very sensitive to the gun pressure and Al flake concentration. Increasing values of XIR reflect a greater degree of alignment of Al particles in the plane of the film surface. Flop value increases with increasing Al particle size while it decreases with increasing Al particle concentration. This trend is opposite to the trend seen with XIR values. Flop is also very sensitive to gun pressure and Al flake concentration.

Spray-coating process and extrusion process parameters have a remarkable influence on the XIR and flop values. The orientation behavior of Al flakes in spray painting is very different than that of extruded films. In spray-coated samples, we can get XIR greater than 3, whereas in extruded polymeric film of ionic copolymer, it was not possible to exceed a XIR value of 2.0 even when changing the processing conditions and characteristics of Al flakes. In the extrusion process, the master batch concentration has little effect on XIR and flop values.

We developed a way to increase XIR values to greater than 2.0 in extruded polymer films by incorporating small amounts of inert platy particles (mica, glass flake). The effect of mica or glass platy particles on XIR and flop values is observed only when the particles are dispersed in EMMA copolymer (Nucrel). Addition of mica flake has greater influence on XIR with Al platelets having sizes in the range of 9.5–14 μm. Flop values do not change with the addition of different amounts of mica to a

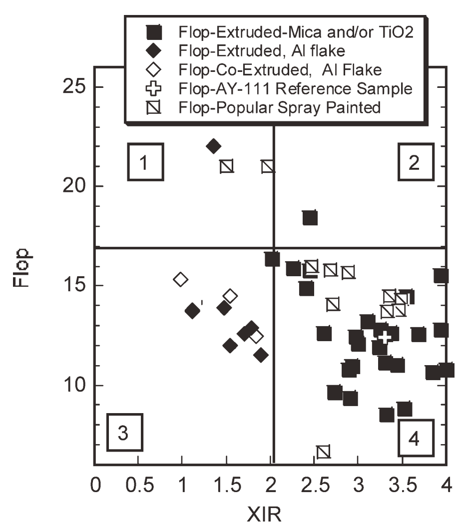

Figure 18 Mapping of metallic look using flop and XIR values of extruded Surlyn® films composed of aluminum particles and other fillers to match metallic look of a spray coated reference sample, AY-111.

sample containing Al flakes having a particle size in the range of 9–25 μm. Therefore, the required flop value can be a decisive factor in choosing the size of Al particle coupled with a particular mica flake concentration. To achieve a flop value of less than 13, we should select an Al flake size smaller than 14 μm, whereas if we desire a flop value of 16, we should choose an Al particle size of 34 μm with addition of 1% mica.

The addition of less than 0.25% spherical particles (TiO_2) to 24 μm Al flake in an ionic copolymer reduces XIR and flop values. Further addition of TiO_2 does not appreciably decrease the XIR values, but continuously reduces the flop values. It is also seen that glass spheres have a similar effect on XIR and flop values (Table III).

The relationships established by coupling XIR and flop measurements were useful for selection of a suitable Al flake from a wide variety of product lines, optimizing process parameters, and determining the composition of blends to achieve a specific value of XIR and flop. It is demonstrated that with our methodology, we can develop extruded film samples that have a visual metallic appearance matching spray-coated reference samples (Fig. 18).

The author is thankful to Rajeev Vaidya, Charles Sobrero, Arun Prakash, and Ram Khanna for the inspiration to complete this work, and to Randy Vogel, Edward Deyrup, John Cheban, Robert Davidson, and Michael Milone, for their help in the experimental work.

References

1. Wissling, P. Metallic Effect Pigments; Fundamentals and Applications (Translated by John Haim and David Hyatt); Vincentz Network GmbH & Co., KG: Hannover/Germany, 2006.
2. Tachi, K.; Okuda, C. J. Coat Technol 1992, 64, 71.
3. Sung, L.-P.; Nadal, M. E.; McKnight, M. E.; Marx, E. J Coat Technol 2002, 74, 55.
4. Wojtkowiak, J. J Paint Technol 1975, 47, 79.
5. Kelly, R. J. U.S. Pat. 1987, 4,692,481.
6. Flynn, M. D.; Truog, K. L. U.S. Pat. 2000, 6,113,838.
7. Smith, H. H.; Sienkiewicz, J. U.S. Pat. 6,319,438 B1, Nov. 20, 2001; US 2002/0009594 A1.
8. Spain, P. L.; Truog, K. L. U.S. Pat. 5,916,643 (1999).
9. Rohrbacher, F.; Spain, P. L.; Fahlsing, R. A. U.S. Pat. 1990, 4,959,189.
10. Mitzutani, H.; Koizumi, J.; Ito, K.; Kobayashi, M.; Isomichi, M. U.S. Pat. 6,280,837 B1. Aug. 28, 2001.
11. Takimoto, M.; Ota, S.; Yamazaki, Y. U.S. Pat. 4,599,376 (1986).
12. Wolf, P.; Pankewitz, W.; Ulmerich, K.WO 99/02594 (1999).
13. Herbert, K.; Easterlow, R. A.; Stephenson, P. J. WO 94/06612 (1994).
14. Helder, V. D. WO 00/06648 (2000).
15. Kurfman, V. B.; Gransden, R. E., Jr. U.S. Pat. 1978, 4,115,619.
16. Morris, M. C.; McMurdie, H. F.; Evans, E. H.; de Groot, J.; Paretzkin, B. Powder Diffraction Data; National Bureau of Standards, Publication DBNBS-1-26, 1st ed., Joint Committee on Powder Diffraction Standards: Pennsylvania, USA, 1976; p 9.
17. Backhouse, A. J. U.S. Pat. 4,403,003 (1983).