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SURFACE HAZE AND SURFACE MORPHOLOGY OF BLOWN FILM COMPOSITIONS*

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ABSTRACT: Reduction in surface haze is a very attractive way to improve the optical properties of most polyolefin films. This route becomes very viable for coextruded multilayer films where the inner layers may be utilized to provide the desired mechanical properties, such as high modulus, controlled shrinkage, and good tear strength while the outer 'skin' layers are utilized to give low surface and total haze values. This study summarizes the effect on surface haze of various such 'skin' layer compositions with a broader goal to produce high clarity and high modulus multilayer blown films. The surface roughness of multilayer films is measured using atomic force microscopy (AFM) and is directly correlated to the measured surface haze of the films.

KEY WORDS: optics, haze, film, multilayer film, polyethylene, LDPE, plastomer, clarity, gloss, AFM, surface roughness.

INTRODUCTION

LOW HAZE, IN combination with high clarity and high gloss, is usually a very desirable optical property for many film packaging applications. The total haze of the film results from scattering of light from primarily two components (a) haze due to scattering from the surface and (b) internal haze due to scattering from the bulk of the polymer. For most thin polyolefin films (<50 μm), surface haze represents the major component out of the total haze. This is especially true for low density

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polyethylene (LDPE) films where the surface haze contribution arising from melt elasticity to the total haze has been reported to be in excess of 90% in many studies [1]. Reduction in surface haze is therefore a very attractive way to improve the optical properties of most polyolefin films. This route becomes very viable for coextruded multilayer films where the inner layers are utilized to provide desired properties, such as high modulus, controlled shrinkage and good tear, etc. while the outer 'skin' layers are utilized to give low surface and total haze values. Walton et al. [2] reported significant reduction in total haze of LDPE films (from 10.1 to 2.7%) by sandwiching the LDPE layer between skin layers consisting of a polyolefin plastomer resin.

Many studies have been done in the past to study the haze properties of polyolefin films. It is important to remember that for light scattering to take place, the size of the defects must correspond with the wavelength of light. As a general rule, if the size of the defects is smaller than $\lambda/20$, the contribution to scattering from those defects is minor. For normal light, which has a wavelength range of 4000–7000 Å, this size scale corresponds to 200–350 Å (20–35 nm). Surface roughness can be due to (a) presence of crystalline structures on the surface, which may result in surface irregularities (crystallite-induced surface haze) and (b) high melt elasticity leading to small-scale melt fracture or orange peel surface (also referred to as extrusion haze). While the influence of surface roughness on optics and haze has been discussed in the literature [1–11], only in a few instances has the actual roughness value of the surface been determined. In the last few years atomic force microscopy (AFM) has been utilized in the literature to determine the surface roughness values and for correlating these values with the haze [3,7,8]. In this regard, Smith et al. [3] investigated four different polyethylene films and found that the roughness value ranged from 18.4 to 28.3 nm for the films that had a surface haze of 4.9–7.6%. We observe that their data did not suggest any strong correlation between surface haze and surface roughness, for the narrow range of films investigated. Ashizawa et al. [11] used a surface profiler and correlated the surface transmittivity with mean surface roughness. Their data suggests a sharp drop-off in surface transmittivity once the surface roughness value exceeded 0.1 μm . However, there does not seem to be any systematic correlation below or above these values.

This article summarizes the effect of surface haze on various skin layer compositions of multilayer blown films. The surface roughness measured on the inside surface of the blown film using AFM is correlated to the measured surface haze.

MATERIALS AND EXPERIMENTAL

Materials

Table 1 lists all the polymers used in the skin layers of multilayer (A/B/A) blown film structures. Since the focus of this article is on surface haze, core layer composition is not relevant. The polyolefin plastomer was produced by The Dow Chemical Company using INSITE¹ Technology. K-13 is a styrene-butadiene block copolymer from Chevron Phillips Chemical Company. This amorphous resin is known to provide stiffness and high clarity.

The three layer blown films were produced using an Egan line having three extruders. The die gap was 50 mil, the layer ratio was 15/70/15%, the production rate was about 225 lb/h (≈ 9 lb/h in. of die circumference) and the melt temperature for each extruder ranged from about 390°F for the LDPE-based formulations to about 450°F for the polyolefin plastomer-based formulations. High molecular weight high density polyethylene (HMW HDPE) film was made on a Kiefel long stalk blown film line. Haze was determined using the ASTM method D1003 and utilizing the Hazegard XL221 Hazemeter by Gardner Instruments. Three specimens were utilized per sample. To determine the internal haze, a clear mineral oil was brushed on both the surfaces, with care being taken to have a uniform smooth coating without any bubbles and brush marks. The surface haze was determined by subtracting internal haze from total haze and then by averaging.

AFM Investigation

Approximately 1 cm² pieces of the inside surface of each film were cut from the sheets and mounted onto a double stick carbon tape supported on steel flats. The samples were then scanned in ambient conditions using MultiMode SPM and a NanoScope IV controller running software version 5.12b15. Nanosensor tips were used in all the experiments. The parameters of the tip were $L = 235 \mu\text{m}$, tip radius = 5–10 nm, spring constant = 37–55 N/m, $F_o = 158.72$ kHz; tapping conditions, tune tip at 3.0 V; drive amplitude, 70–80 mV, moderate tapping. It was found that the surface roughness measured using AFM depended somewhat upon the scan size as seen from Figure 1. Data in Figure 1 are for a

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Table 1. Polymers used in skin layers.

Skin layer composition	Melt index (190°C, 2.16 kg)	Density (g/cc)
K-13	1.10	1.05
LDPE A	1.9	0.922
LDPE B	2	0.924
Z/N LLDPE	1	0.920
Metallocene LLDPE	1	0.917
Polyolefin plastomer	1	0.909
Random copolymer polypropylene (RCP)	7 (MFR)	–

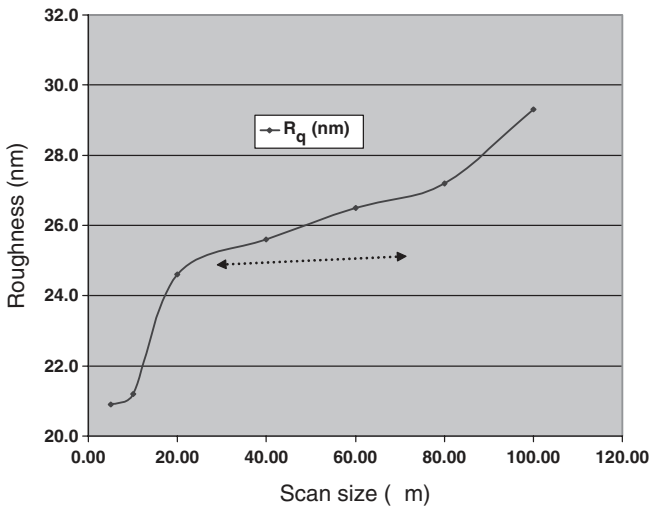


Figure 1. Measured surface roughness as a function of scan size.

representative LDPE blown film. Scan size of $40 \times 40 \mu\text{m}^2$ was used in this study to measure the surface roughness.

Definitions of R_a , R_q , and R_{max}

- R_q is the geometric mean deviation of all the points on the surface from the mean value of the data. It is also called the RMS or root-mean-squared roughness.

$$R_q = \left[\frac{\sum (Z_i - Z_{ave})^2}{N} \right]^{1/2}$$

- R_a is the arithmetic mean deviation of the actual surface relative to the center plane fit to the data.

$$R_a = \frac{\sum(Z_i - Z_{cp})}{N}$$

- R_{max} is the difference in height between the highest and the lowest points on the surface relative to the mean plane.
- Delta SA is the difference in surface area between the imaged surface and a flat surface of the same lateral size, expressed as a percentage.

Here, Z_{ave} is the average Z value within the given area, Z_{cp} is the Z value of the center plane, Z_i is current Z value, and N is the number of points within a given area (512×512).

Note that the surface roughness of the inside and outside layers of the blown film would be somewhat different due to differences in thermal history experienced. In this study, the surface roughness of the inside layer is correlated to the surface haze of the film, which is a sum of the haze of the outside and inside surfaces of the blown film. Surface roughness was not measured on the outside surface of the film as it was felt to be distorted by nip rolls.

RESULTS AND DISCUSSION

Surface Haze and Surface Morphology of Various Skin Layers

Controlling the skin layer composition and hence the surface haze is considered to be a very important step in achieving the high clarity compositions. Surface haze results for various skin layers and the corresponding surface morphologies of those surfaces are presented. Results for some additional film resins, such as HMW HDPE are presented for comparison.

For the various film compositions utilized in this study, the surface haze and surface roughness values are presented in Table 2. Figures 2–11 reveal the surface profile scans of a $40 \times 40 \mu\text{m}^2$ area with the height scale being 400 nm/division. The following describes the effect of various skin layer compositions on surface haze.

Table 2. Results for surface haze and surface roughness for various skin layers.

Skin layer composition	Surface haze (%)	R_a (nm)	R_q (nm)	R_{max} (nm)	$\Delta SA\%$
K-13 copolymer	1.10	10.5	13.6	155.6	0.27
LDPE A	4.65	19.9	24.9	210.4	0.79
LDPE B	5.70	21.8	28.1	261	0.79
Z/N LLDPE	9.35	29.0	37.2	591	1.56
LDPE A (20%)/Z/N LLDPE (80%)	3.05	17.4	22.3	214.1	0.82
LDPE A (20%)/metallocene LLDPE (80%)	4.20	19	24.3	372.8	0.99
Polyolefin plastomer	2.45	16.9	21.4	234.7	0.30
RCPP	2.66	16.7	21.3	221	0.33
HMW HDPE	74.30	220.2	278.9	1773	3.09

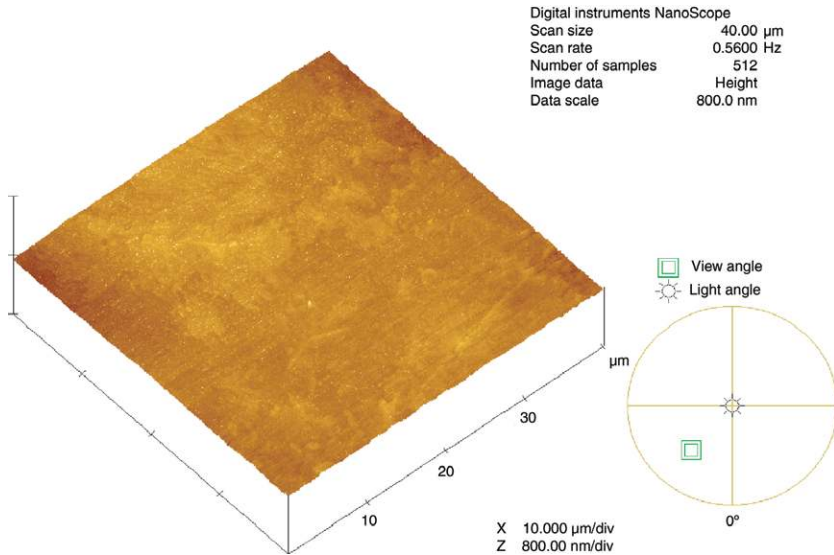


Figure 2. Surface profile of the styrene-Butadiene (K-13) blown film surface.

K-13 Resin, a Styrene-Butadiene Copolymer

It was observed that the surface haze for the K-resin is very low at 1.1%. This amorphous resin does not contribute any crystallinity-induced haze to the surface haze. The low surface haze also indicates that melt elasticity did not lead to any significant fine scale melt fracture for this resin. The surface profile of this resin (Figure 2) clearly confirms

the existence of a very flat and smooth surface and explains the reason for the low haze value.

LDPE A and LDPE B

These two clarity grade LDPE resins were similar in both their surface roughness values and the contribution due to surface haze. Surface haze was 4.65% for LDPE A and 5.70% for LDPE B. See Figures 3 and 4 for surface profile.

Blend of 20% LDPE A and 80% Z/N LLDPE

The surface haze for the blend of 20% LDPE A and 80% Z/N LLDPE was 3% and was lower than surface haze for either LDPE A (surface haze = 4.65%) or Z/N LLDPE (surface haze = 9.35%) by itself. The surface profile of 100% Z/N LLDPE sample is shown in Figure 5. The addition of the small amount of LDPE is effective in breaking up the crystalline morphology of the pure Z/N LLDPE resulting in smoother surface and hence, lower surface haze (see Figure 6 for the surface profile of this composition). Note that the LDPE resin chosen as the blend component is a clarity LDPE grade and would not increase the extrusion haze component of surface haze.

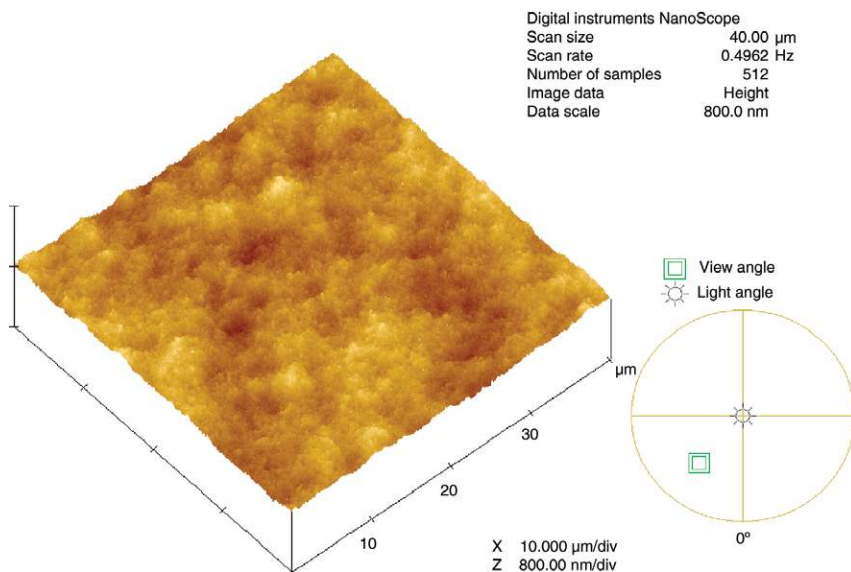


Figure 3. Surface profile for the LDPE A blown film surface.

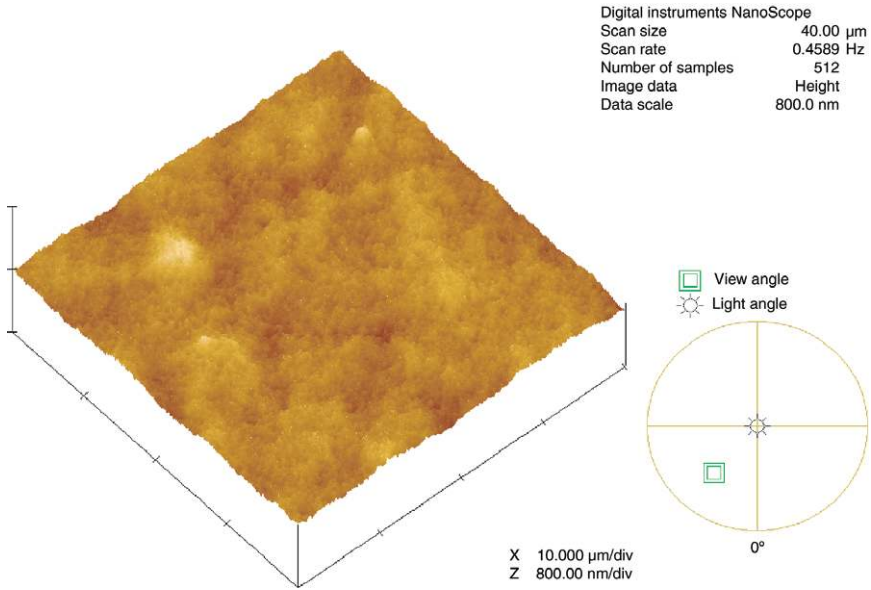


Figure 4. Surface profile for the LDPE B blown film surface.

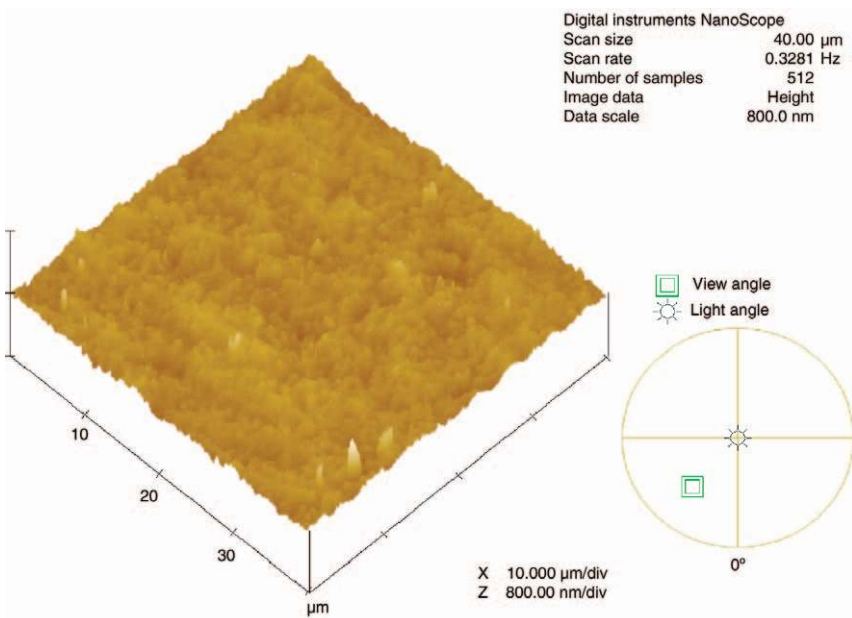


Figure 5. Surface profile of Z/N LLDPE blown film surface.

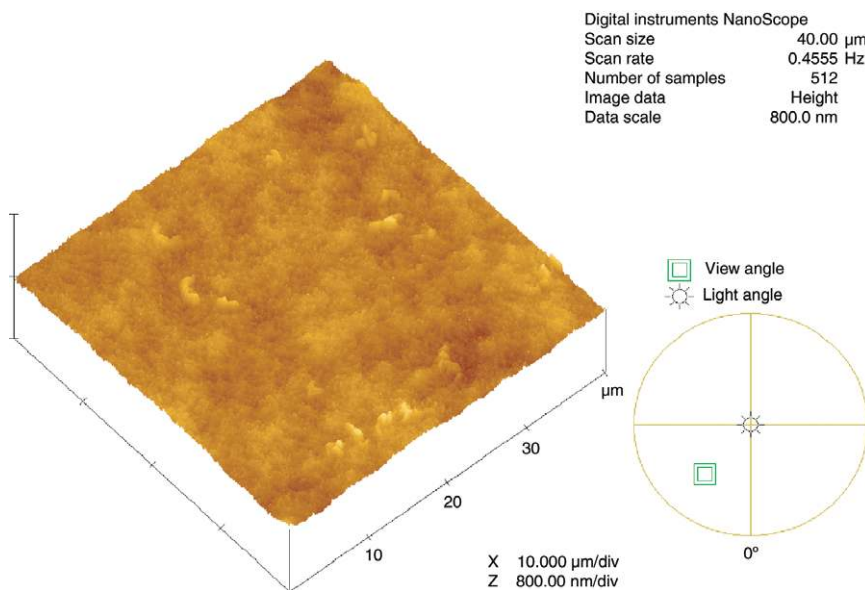


Figure 6. Surface profile of 20% LDPE A 80% Z/N LLDPE film surface.

Blend of 20% LDPE A and 80% Metallocene LLDPE

The blend of 80% metallocene LLDPE and 20% LDPE A was investigated as skin layers in our study. Metallocene LLDPE was made using supported metallocene catalyst in a gas-phase process. It exhibited narrow molecular distribution and narrow composition distribution. Blown film from such metallocene LLDPE films are known to exhibit high total haze [9,10]. This is because the metallocene LLDPE exhibits low melt elasticity and fast relaxation times due to narrow molecular weight distribution and lack of long-chain branching, allowing quiescent type spherulitic like morphology to develop in a blown film [9]. These 'spherulitic-type' structures then lead to high surface roughness and hence, high surface and total haze. However, addition of small amount of LDPE resin in metallocene LLDPE reduced total haze and surface haze significantly. Addition of long-chain branches (by adding LDPE) increased the average relaxation time and hindered the development of large spherulitic-type superstructures that are responsible for the high haze in the neat metallocene LLDPE resins. The surface haze of the blend was 4.2% and Figure 7 shows the

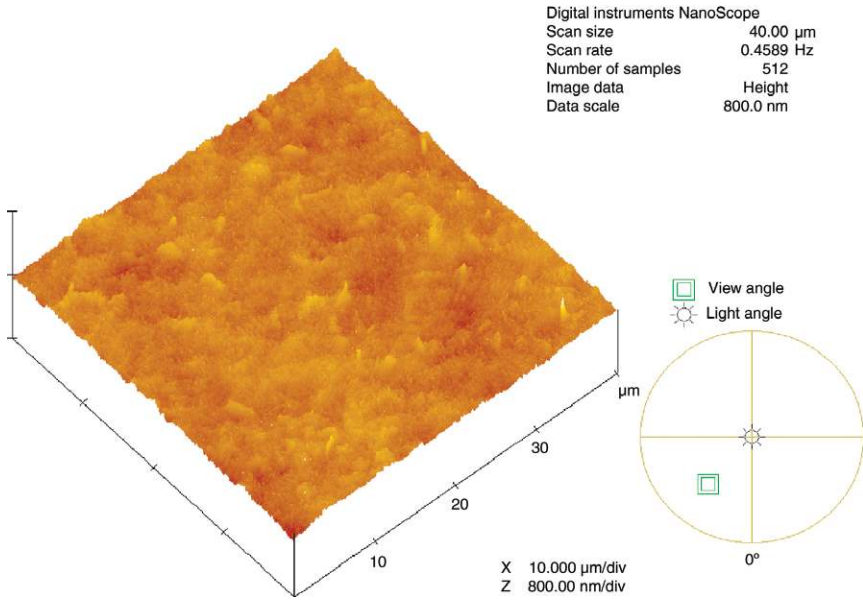


Figure 7. Surface profile of LDPE A (20%)–metallocene LLDPE (80%) blown film surface.

roughness profile. Note also that the neat metallocene LLDPEs do not typically exhibit extrusion-induced surface haze (generally induced due to presence of high molecular weight tail or high level of long-chain branching) as evidenced by the clear molten bubble before the onset of crystallization (frost line) and the high haze in the final film.

Polyolefin Plastomer

The surface haze for the polyolefin plastomer skin-layer resins was low at 2.45%. This corresponded very well with the low surface roughness values and the surface profile shown in Figure 8. Owing to the low density, the crystalline contribution to surface roughness is low. This particular polyolefin plastomer did have a small amount of LCB; however, it was not enough to contribute significantly towards the surface roughness (i.e., compared to traditional LDPEs). These data show that polyolefin plastomer is a good candidate for skin layers where low surface roughness is desired. Compared to Z/N LLDPE and LDPE resins, the polyolefin plastomer has a lower melting resin and hence can provide low heat seal temperatures.

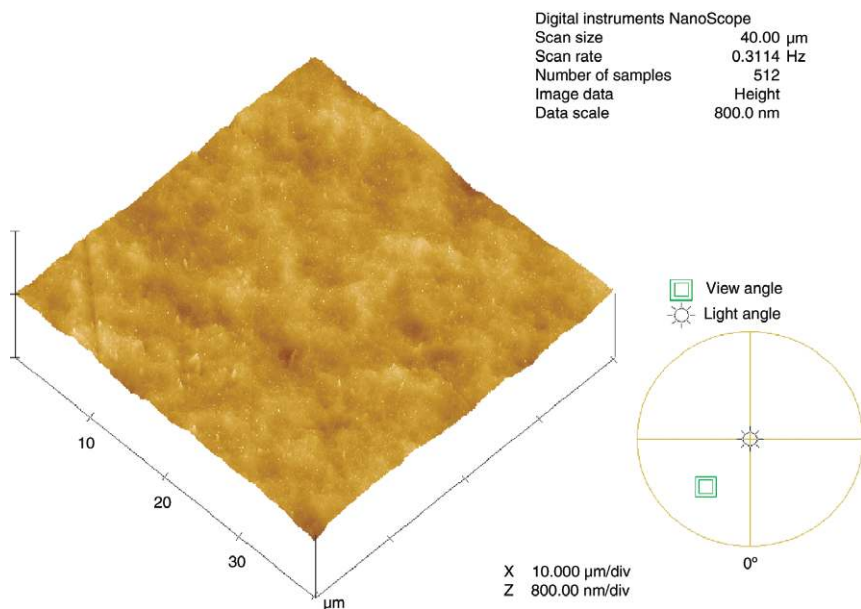


Figure 8. Surface profile of the polyolefin plastomer blown film surface.

Random Copolymer Polypropylene (RCP)

The use of RCP as a skin layer was explored for the multilayer compositions. The surface profile of this ethylene-based RCP is shown in Figure 9. The results indicate that RCP can be an excellent candidate if low surface roughness is desired; the data for surface haze and surface roughness values are very similar to that of the polyolefin plastomer resin. The use of RCP leads not only to higher modulus but also to higher heat seal initiation temperatures.

HMW HDPE Monolayer Blown Film

The surface roughness profile of a HMW HDPE blown film is shown in Figure 10. The HMW HDPE resin had a melt index at 5 kg load (I_5) of about 0.4 and a density of about $0.950 \text{ g}/\text{cm}^3$. The blown film exhibited a very rough surface. This is mainly because the film was made from a very high molecular weight and a very broad molecular weight distribution HDPE resin having very high melt elasticity. High melt elasticity is known to cause high level of surface roughness as the melt exits a blown film die [10].

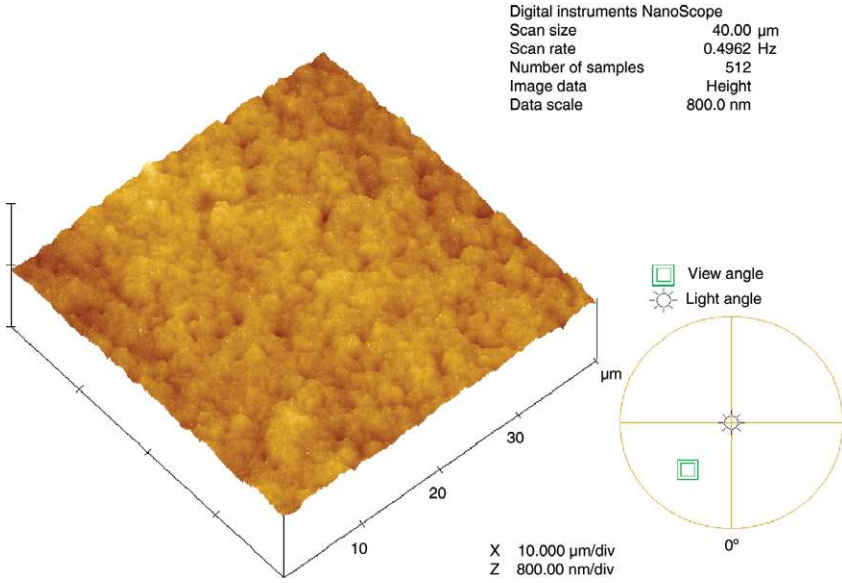


Figure 9. Surface profile of the RCP blown film surface.

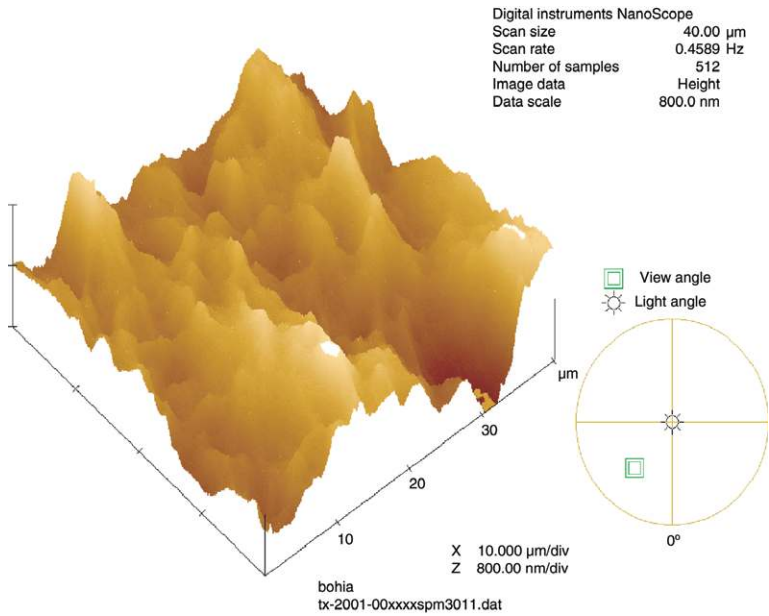


Figure 10. Surface profile of the HMW HDPE blown film surface.

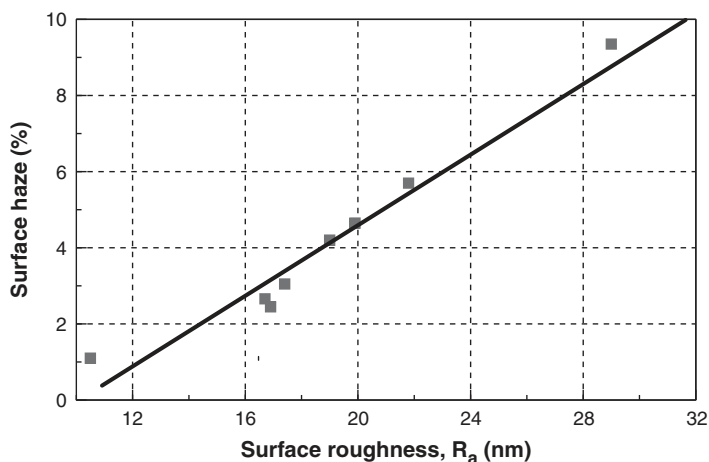


Figure 11. Surface haze vs surface roughness (R_a) of multilayer blown films.

Correlation between Surface Roughness and Surface Haze

This study and other literature suggest that AFM can be a very useful tool to study the surface roughness across a broad range of surface roughness. The surface profile scans are especially useful in the visualization of the surface roughness and for direct comparison. The correlation of AFM average surface roughness data to haze values is shown in Figure 11. An excellent correlation between surface roughness measured by AFM and surface haze values is revealed.

CONCLUSIONS

Reduction in surface haze is a very attractive way to improve the optical properties of most polyolefin films. For co-extruded multilayer films, this route becomes even more attractive as the inner layers in these cases can be utilized to provide desired properties, such as high modulus, low shrinkage, and high tear strength, while the outer (skin) layers can be utilized to give low surface and total haze values. AFM images clearly differentiated large differences in surface haze of various skin layers. An excellent correlation between AFM roughness data and surface haze was found.

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BIOGRAPHIES

Rajen Patel

Rajen Patel joined the material science group of The Dow Chemical Company after completing his PhD in Polymer Science and Engineering at the University of Tennessee, Knoxville in 1991. He has worked on various projects involving polyolefins characterization (thermal and rheological), material science and product development, including oriented shrink films, sealants, cast stretch films, blown films, elastic films, and fibers. Rajen has written a chapter on structure-properties and applications of polyolefins produced by single-site catalyst technology and has co-authored about 15 peer reviewed journal publications. He is co-inventor of about 15 US patents and is currently a research leader in the plastics materials science group in The Dow Chemical Company.

Varun Ratta

Varun Ratta earned his BSChE from IIT (Kharagpur) and his PhD in Chemical Engineering from Virginia Tech. He joined Dow Plastic's materials science group after his post-doctoral studies at Virginia Tech. He led projects in the area of polyolefin stretch films, blown films, and heavy duty polyolefin applications. Varun moved on to support application development projects related to a novel polyolefin elastic fiber, Dow XLA. He is currently responsible for the Dow XLA projects and customers in North America.

Pepe Saavedra

Pepe Saavedra graduated from Texas A&M with a BSChE in 1977. He then worked at Dow in process engineering, polyurethanes research, and with epoxy materials. Since 1992, Pepe has worked in TS&D for polyolefins film applications in Latin America (North region).

Jing Li

Jing Li received her BS Chemistry from Jilin University and PhD in Chemistry from Changchun Institute of Applied Chemistry. She joined Michigan Molecular Institute at Midland, Michigan for her postdoctoral research in 1995, where she was involved in research projects of latex deformation, coating surface morphology, and dendrimer characterizations. In 1999, Jing joined the Center for Biologic Nanotechnology at Medical School, University of Michigan as an investigator to lead scanning probe microscopy (SPM) technology for the characterization of nanomaterials. She joined The Dow Chemical Company in 2000 and has been leading the SPM effort to support Plastic R&D involved in research, methodology development, and characterization of polymer materials. Jing has over 36 publications and is now a senior analytical specialist and an SPM team leader.