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Effect of Material Structure and Additives on the Optical Properties of *PP* Cast Films

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Summary. Polypropylene homopolymer and ethylene/propylene-random-copolymer cast films formulated with slip, anti-blocking, and acid scavenger aids were analyzed as to material structure and optical properties. The structural and topographical characterization was done by atomic force microscopy and by spectroscopic methods. Optical properties were determined using a hazemeter and an UV/VIS/NIR spectrophotometer. As to the effect of additives it was established that slip and anti-blocking aids migrate to and accumulate on the surface, resulting in increased surface roughness and larger scattering identities close to the surface. Acid scavenger additives were shown to contribute to less significant slip aid domains and hence to lower haze. In general, films without additives showed much better optical properties. The separation of haze into its bulk and surface components revealed that the total haze is dominated by surface haze.

Keywords. *PP* cast films; Surface; Structure elucidation; Spectroscopy; Haze.

Introduction

Due to technical and economic reasons polypropylene (*PP*) is today one of the materials of choice for packaging applications in the medical industry. To meet the high requirements in the packaging of drugs and of medical substances in particular, *PP* films have to exhibit outstanding optical properties.

As various earlier studies [1–4] pointed out, disturbances affecting the optical properties of melt processed semi crystalline films can be ascribed mainly to surface irregularities, caused by crystallization and/or extrusion. Whereas the former

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can be attributed to the formation of crystalline aggregates on or close to the surface, the latter is ascribed to the rheological characteristics of the melt [1, 2]. In various previous [1–3, 5] and recent [6–10] studies a comprehensive understanding of the mechanisms of haze in polymer films for packaging applications was established, by investigating the effects of molecular weight, molecular weight distribution, chain branching, rheological properties (shear strain, melt flow rate), mechanical properties (relaxation time, elasticity), orientation, processing conditions, and cooling rate on the formation of scattering identities. *Lin et al.* [11] and *DeMeuse* [12] studied the processing behavior and optical properties of *PP* cast films synthesized with metallocene catalysts. It was shown that a narrower molecular weight distribution leads to a more uniform crystal size distribution and thus to lower surface roughness and reduced light scattering.

Some recent publications [13–16] investigated the influence of additives on the surface and optical properties of blown films. As polyolefin films generally tend to stick together, for easier processing and handling of the films it is necessary to add special additives such as slip and anti-blocking aids. Over time these additives migrate to and accumulate on the surface creating a micro-roughness [16, 17]. This in turn reduces the adhesion between film layers indeed, but contributes to worse optical properties as well. The deterioration of haze can be attributed to light scattering both due to differences in refractive index in the bulk and to reflection and refraction effects at the surface. Common anti-blocking aids such as synthetic silica are today harmonized with slip aids like fatty acid amides, providing a balance between desired blocking and optical properties of the films [13, 16].

While in *Resch et al.* [18] characterization methods such as high-resolution microscopy and X-ray scattering as well as technological methods such as haze and clarity measurement techniques were used to perform a comprehensive investigation of the topography, morphology, and optical properties of *PP* cast films produced from different polymer types and formulated with various amounts of slip, anti-blocking, and acid scavenger aids, within this paper an additional focus is given to spectroscopic characterization methods to obtain a detailed understanding of the material structure on the surface and of the wavelength and position dependent scattering mechanisms.

Results and Discussion

Topographical Structures of the Films

A representative $50 \times 50\,\mu\mathrm{m}^2$ atomic force microscopy (AFM) height image of a homopolymer film without slip and anti-blocking aid and produced under soft box condition high is shown in Fig. 1.

The characteristic feature of the height images of the films without additional aids are 8-shaped structures with a preferential orientation aligned in machine direction. The structures consist of two adjacent lower centers, surrounded by an elevated ring. Their dimensions are in the order of a few microns. It was found that the 8-shaped structures appear much more frequent and are slightly smaller for soft box condition high, especially on the top surface which is cooled by airflow from the soft box. This fact as well as oriented lamellae in the elevated ring, detected

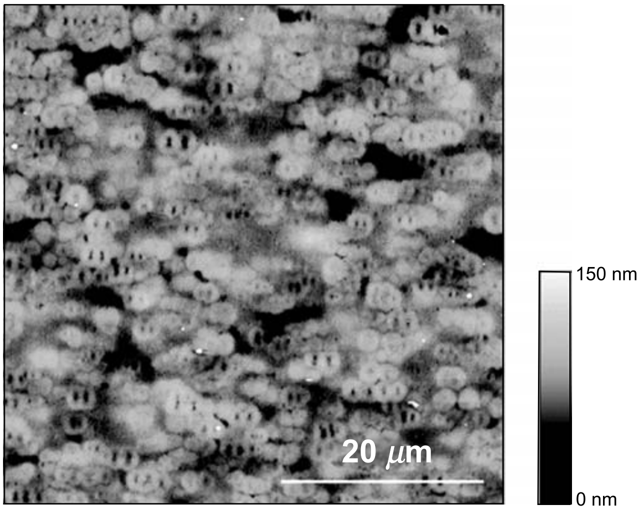

Fig. 1. $50 \times 50\,\mu m^2$ AFM topographic images of a homopolymer film type formulated without slip, anti-blocking, and acid scavenger aids

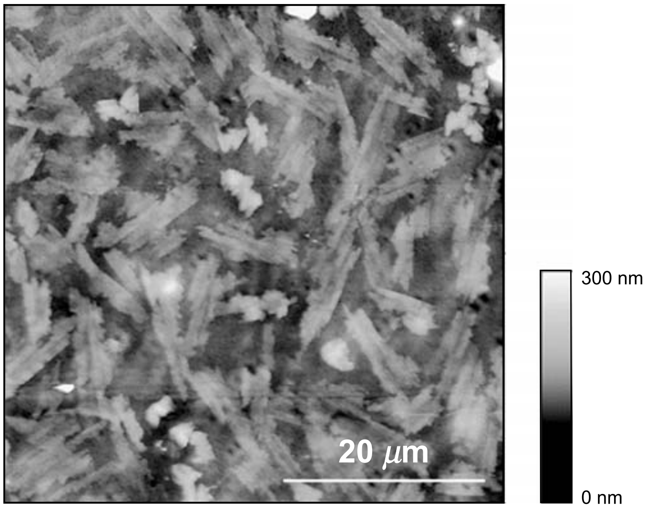

Fig. 2. $50 \times 50\,\mu m^2$ AFM topographic images of a copolymer film type formulated with slip and anti-blocking aids

with phase imaging AFM indicates that the features represent a kind of spherulitic-like superstructure [18].

Figure 2 shows a representative $50 \times 50\,\mu m^2$ AFM height image of a copolymer film type formulated with slip and anti-blocking aid and produced under soft box condition high.

Randomly distributed plate-like or layered as well as smaller more or less spherical particles are observable. The 8-shaped structures are scarcely appearing. To determine whether the plate like structures can be attributed to the slip or to the anti-blocking aid attenuated total reflection-spectroscopy was carried out. The representative spectrum is shown in Fig. 3.

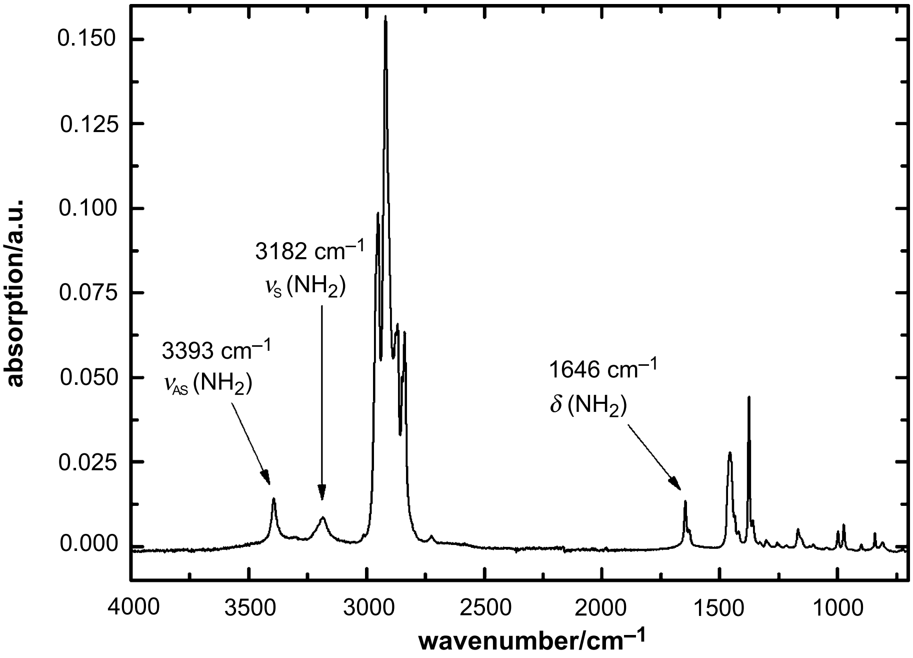

Fig. 3. ATR spectrum of film type 4H (copolymer; formulated with slip and anti-blocking aids; produced under soft box condition high)

Besides the typical *PP* peaks significant absorption bands at 1646, 3393, and 3182 cm^{-1} were detected, which can be attributed to bending, asymmetrical stretching, and symmetrical stretching vibrations of amide groups, respectively. As the silicon oxide groups of the anti-blocking aid occur rather insignificant in the recorded spectra, the prevalent plate-like, layered structures can be ascribed to crystallized erucamide slip agent. Similar plate-like erucamide crystals detected by AFM are described in the literature [17]. By Infrared (IR) spectroscopy of the 50 μm thick film in transmission mode (Fig. 4) neither amide nor silicon oxide absorption bands were detectable. As IR spectroscopy maps the chemical composition across the film thickness, it can be concluded that the slip agent migrates to and accumulates on the surface.

An AFM height image of a copolymer film formulated with slip, anti-blocking, and acid scavenger aid is depicted in Fig. 5.

As already described above for a film type containing slip and anti-blocking agent, also spherical domains with greater height differences to the matrix and plate-like structures are observable. However, in comparison to film types 4 without acid scavenger aid, the stearate acid scavenger agent may contribute to a less significant development of erucamide domains on the film surface. Furthermore no 8-shaped structures were identified. The ATR spectrum (see Fig. 6) shows besides the stretching and bending vibrations of the amide groups a weak ester absorption band at 1728 cm^{-1}, which can be attributed to the stearate acid scavenger agent.

Although the study of *Catino et al.* [16] pointed out that surface enrichment of additives does not necessarily correlate with surface height and hence surface roughness, a significantly enhanced surface roughening due to the additives was

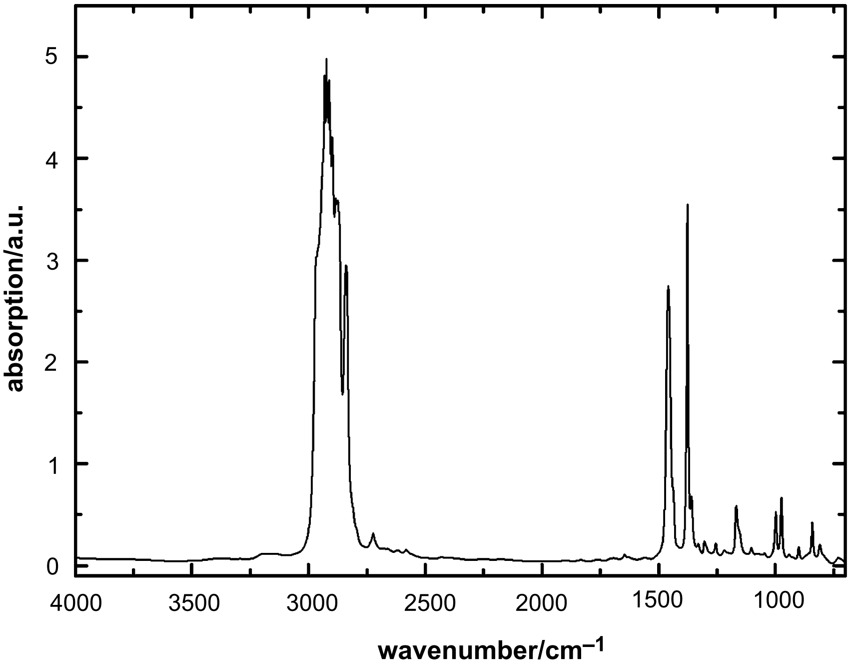

Fig. 4. IR spectrum of film type 4H (copolymer; formulated with slip and anti-blocking aids; produced under soft box condition high)

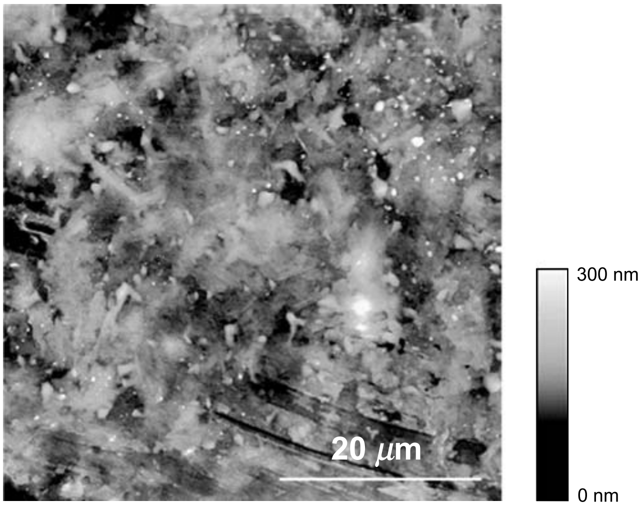

Fig. 5. $50 \times 50\,\mu\text{m}^2$ AFM topographic images of a homopolymer film type formulated with slip, anti-blocking, and acid scavenger aids

detected within the present study. While film types without slip, anti-blocking, and acid scavenger agents exhibit root-mean-square roughness values of about 10 nm, the vertical roughness is about twice as high for the films with slip and anti-blocking aids. A detailed discussion of the surface roughness parameters as well as of surface structure is described in *Resch et al.* [18].

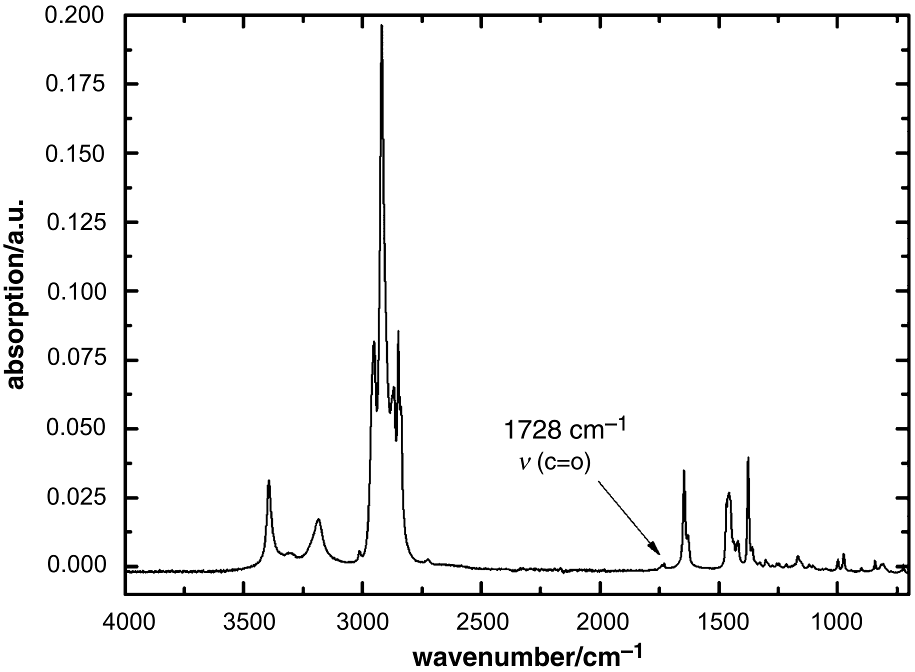

Fig. 6. ATR spectrum of film type 5H (copolymer; formulated with slip, anti-blocking, and acid scavenger aids; produced under soft box condition high)

Optical Film Properties

In Fig. 7 diffuse transmittance spectra over the solar wavelength range of the films produced under soft box condition low (L) are shown. The spectra reveal significant differences in the scattering behavior of films without (1L and 2L) and with additional aids (3L, 4L, 5L).

While for the films without additional aids the diffuse transmittance values are over the whole wavelength range below 0.05 only slightly increasing with decreasing wavelength, for the films with additional aids a significant increase of the diffuse transmittance values in the short wavelength range was found associated with also higher diffuse transmittance values in the near infrared wavelength range. Thus, more and also larger scattering domains are active in the films with additional aids. A comparison of film types 4 and 5 clearly indicates that the addition of the acid scavenger aid reduces the diffuse scattering power. This is in good agreement with the smaller domain size in the AFM height image on the surface of the acid scavenger modified film type.

As to the refractive index, values between 1.48 for material type 1 and 1.52 for material type 5 were obtained. Thus, a matching liquid with a refractive index of 1.51 was chosen for all film types for further investigations.

Total haze values of the investigated films determined by hazemeter and spectrophotometer are compared in Fig. 8.

The haze values determined with the spectrophotometer are slightly higher than those determined with the hazemeter, what can be attributed to the smaller opening angle of the light trap used in the spectrophotometer (2°). Nevertheless, with both

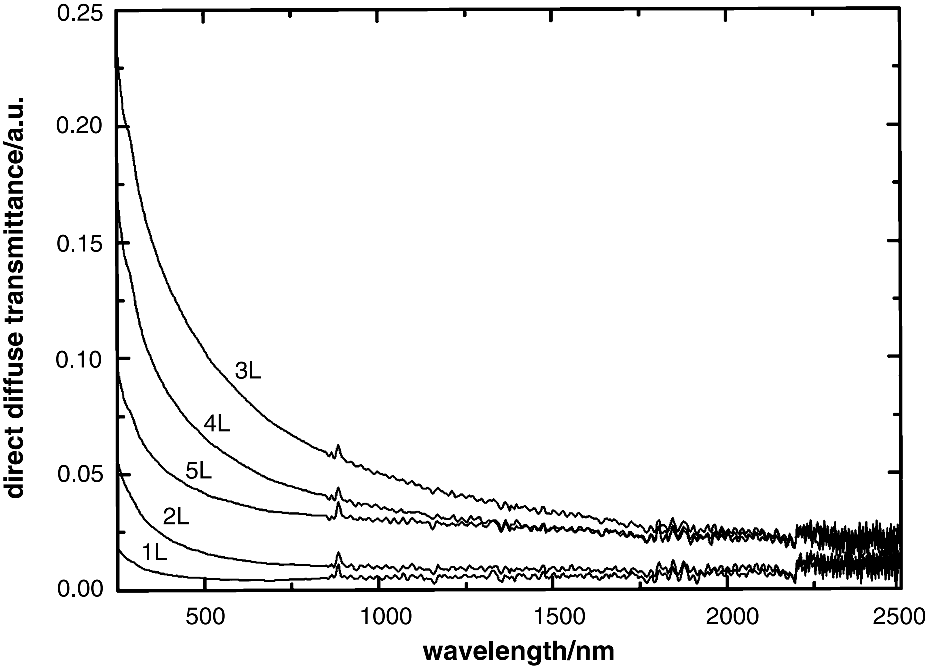

Fig. 7. Diffuse transmittance spectra of film types produced under soft box condition low (abbreviations are given in Table 1)

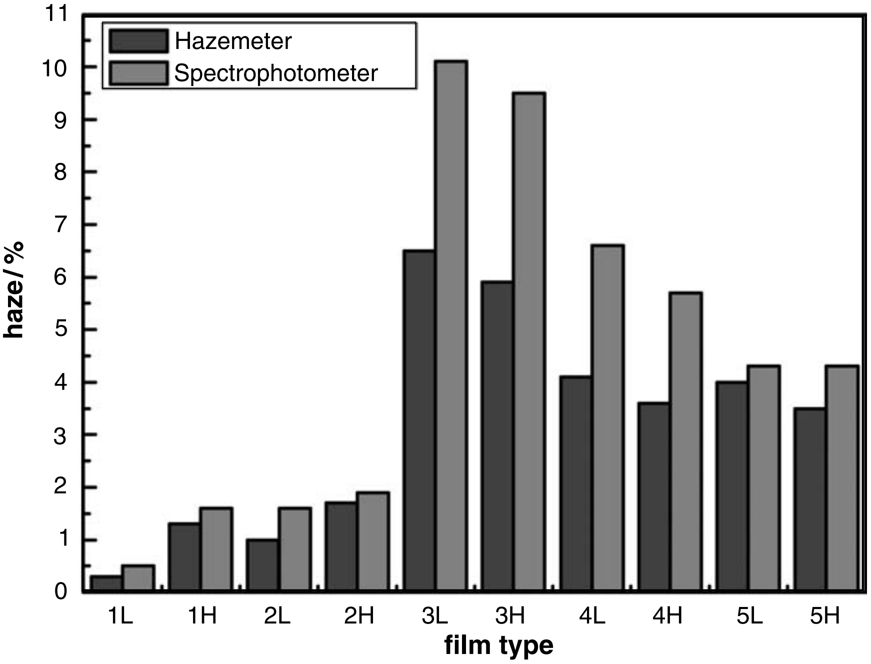

Fig. 8. Haze values of the investigated films determined using a hazemeter and a spectrophotometer (abbreviations are given in Table 1)

measurement techniques the same interrelationships between material structure and processing conditions were obtained. It can be seen that haze is excellent for the films without additional aids. There is a tendency that the homopolymer films show better optical properties than the copolymer films, which may result from the difference in melt flow rate and therefore in molecular weight, which is lower for the homopolymer materials. Slip, anti-blocking, and acid scavenger aids affect the optical properties considerably, as haze is significantly increased. For the films with additional aids, the copolymer films show better optical properties. Figure 8 further illustrates that processing conditions have a significant impact on optical properties. In general an increase in soft box condition results in worse optical properties for the film types without additives. In contrast, an enhanced soft box airflow leads to an improvement of haze values for the films with slip and anti-blocking aids.

In Fig. 9 total, surface, and bulk haze of the films without the additional aids are exhibited.

For all film types almost the same values for bulk haze were determined, indicating clearly that total haze is dominated by surface haze, which is strongly dependent on processing conditions. While the fraction of surface haze (defined by the ratio surface to total haze) is about 60% for the films without additional aids produced under soft box condition high, it is only about 40% for the films produced under soft box condition low. For the film types with additional aids (Fig. 10) the surface fraction of haze is always higher than the bulk fraction, independent of the processing condition. The values vary between 80 and 85%.

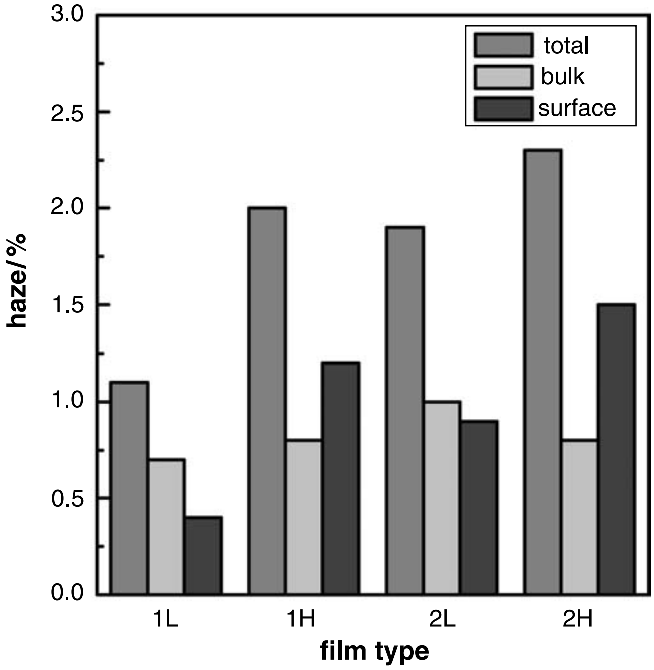

Fig. 9. Total, bulk, and surface haze of the films formulated without additional aids (abbreviations are given in Table 1)

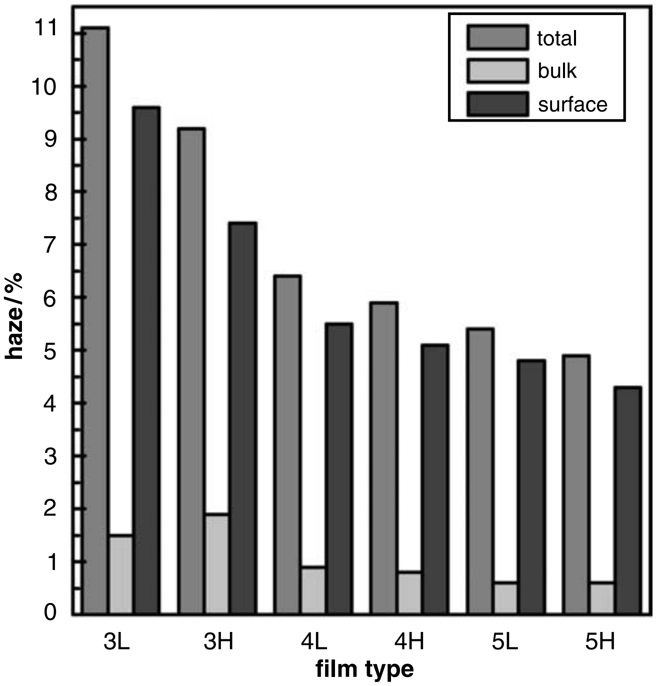

Fig. 10. Total, bulk, and surface haze of the films formulated with slip, anti-blocking, and acid scavenger aids (abbreviations are given in Table 1)

Again, the bulk haze values are almost the same for the films produced from the same material type but under different processing conditions. This fact as well as the excellent linear correlation of haze with surface roughness parameters as shown in *Resch et al.* [18] point out the role of the surface in diffuse scattering. For the example of highly transparent *PP* cast films it was shown that haze is mainly affected by light scattering due to surface roughness effects, whereas the film bulk plays a minor but non the less important role, particularly for films formulated without slip and anti-blocking aids.

Experimental

Materials

PP types and formulation parameters of the materials investigated are summarized in Table 1.

All resins were based on standard 4th generation catalyst systems and were formulated with an antioxidant. In selected material types erucamide slip agent, synthetic silica anti-blocking aid, and calcium stearate acid scavenger aid coated on silica were added. Further details as to resin properties and structure are given in *Resch et al.* [18].

The resins were extruded into $50\,\mu$m thick cast films with an industrial scale extruder equipped with a 6-section screw with a dispersive mixer and a soft box. The soft box allows for a controlled attaching of the film to the chill roll immediately after the extrusion die and is further used for the cooling of the upper film surface. For comparison purposes two soft box conditions were applied within the present study. Films were produced under soft box condition low with a weak airflow and under soft box condition high with an increased airflow. As to the nomenclature, L and H indicate soft box condition low and high, respectively. The die-zone temperature was about 250°C. The output rate was approximately 600 kg/h.

Table 1. *PP* types and formulation parameters of the films

Film type	*PP* type	Soft box condition	Slip aid	Anti-blocking aid	Acid scavenger aid
1L	homopolymer	low	−	−	−
1H	homopolymer	high	−	−	−
2L	copolymer	low	−	−	−
2H	copolymer	high	−	−	−
3L	homopolymer	low	+	+	−
3H	homopolymer	high	+	+	−
4L	copolymer	low	+	+	−
4H	copolymer	high	+	+	−
5L	copolymer	low	+	+	+
5H	copolymer	high	+	+	+

Topographical and Spectroscopic Characterization

The film surface and topography was characterized with a NanoScope Multi Mode (Digital Instruments, California, USA) Atomic Force Microscope operating in tapping mode (frequency: 250–300 kHz). Sharpened Si NCH tips with a tip radius <10 nm and an opening angle of 18° were used. Prior to the measurements the polymer films were cut into disc-shaped samples, glued on a metallic sample holder with a double-sided tape, and stored at 23°C for 24 h at a humidity of 50% to avoid electrostatic charging.

To obtain information as to chemical composition and structure of the materials investigated FT-IR spectroscopy was performed in a wavenumber range from 700 to 4000 cm^{-1} at a resolution of 2 cm^{-1} (Spectrum One, Perkin Elmer Instruments GmbH, Überlingen, GER). To characterize the structure on the film surface IR spectroscopical measurements were carried out in attenuated total reflection (ATR) mode applying a contact force of 100 N. The obtained spectra were corrected for the wavelength-dependent penetration depth of the evanescent wave as well as for the baseline by the *Spectrum v. 5.0* software (Perkin Elmer Instruments GmbH, Überlingen, GER).

Determination of Optical Properties

The characterization of the optical properties was carried out using a hazemeter as well as a spectrophotometer. Applying the BYK-Gardner Hazegard Plus Instrumentation (BYK-Gardner, Columbia, USA) it was focused on the determination of total haze. The samples were illuminated with standard illuminant C and haze was considered as that fraction of transmitted light, which is scattered in the forward direction between 2.5° and 90°. However, no differentiation was done as to the surface and bulk contribution of haze.

To separate the total haze into its bulk and surface componentes an UV/VIS/NIR spectrophotometer (Lambda 950, Perkin Elmer Instruments GmbH, Überlingen, GER) was used. First, hemispherical and diffuse transmittance spectra within the wavelength range from 300 to 2500 nm were recorded. Subsequently, based on *Maheu* and *Gouesbet* [19] the materials refractive indices were evaluated from the hemispherical transmittance spectra at a wavelength of 635 nm assuming no scattering losses. Referring to these data, silicon immersion oil with matching refractive index (A-series oil with refractive index 1.51, Cargille Laboratories INC, New Jersey, USA) was selected for the determination of bulk haze.

According to a procedure described by *Stehling et al.* [1] and more explicitly by *Ashizawa et al.* [2] and *Bheda* and *Spruiell* [3] the films were first clamped between two microscope slides to determine the total haze of the films. Second, the films were coated with silicon immersion oil on both sides and again clamped between two microscope slides. As the oil compensates for surface roughness the recorded spectra represent the optical properties of the bulk solely. To eliminate errors originating from these measurement setups the recorded spectra were corrected by the scattering spectrum of merely two slides without a film in between and by a spectrum of the two slides with just the immersion oil in between, respectively. From the obtained results haze was calculated weighting the data recorded within the visible wavelength range by the spectral data of standard illuminant C. The difference between total and bulk haze provided surface haze directly. It should be noted that in the case of the spectrophotometric measurements haze was considered as that fraction of transmitted light that deviates from the incident beam by more than 2°.

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