Introduction Polypropylene (PP) is one of the most preferred polymer in food packing, protective coating and printing applications with its high stifness, high temperature resistance, good chemical resistance, lower moisture transmission rate and high mechanical stress properties [1-4]. The polypropylene film that is stretched in both machine direction (MD) and across machine (transvers) direction to improve mechanical properties is called biaxially oriented polypropylene (BOPP). BOPP is widely used in packaging and in a variety of other applications due to their great potential in terms of barrier properties, brilliance, dimensional stability and processability [2]. Different fillers such as talc and calcium carbonate and pigments may be added to BOPP films in order to improve its optical properties and provide a pearly aesthetic look [5, 6]. Thus flexible packaging companies are willing to use pearl films for their inexpensive prices, good decoration, and excellent performance. Generally, because they have a certain pearl effect, they are often used in cold drink packaging such as: ice cream, heat seal label, sweet food, biscuits, and local flavor snack packaging [1]. Mineral particles, such as calcium carbonate and talc powders, are widely used in biaxially oriented films, which are also called cavitated and pearlized structures. Pearled film is based on orientation process, where the interface around the particles is stretched forming small cavities in the polymer structure. The foam extent of the film is low but the film becomes highly opaque because of inter scratches [4, 7, 8]. Pearl film is a kind of BOPP film by adding pearl pigments into plastic particles and through biaxial stretch heat setting. A typical pearl film is BOPP pearl film produced by A/B/A layer co-extruded biaxial stretch [9]. Three layer films are coextruded where the surface is optimized in order to attain good printability. In fact, the more pigment is in the system the more light is scattered outward, making the system appear opaque and white [10]. Calcium carbonate particles having 0.7-3 µm size are often used in producing micro porous films [11]. The surface morphology of BOPP film could be investigated by atomic force microscopy. The polymer film is characterized by a nanometer-scale, fiberlike network structure, which reflects the drawing process used during the fabrication of the film. the residual effects of the first stretching of the film surface can provide information on the way in which morphological development of the BOPP occurs [12, 13]. The aim of the present study is characterization of a commercial pearlescent BOPP film by advanced analytical techniques. The functional groups, crystal structure, morphology and surface roughness were investigated. Experimental Materials The pearlescent films that were kindly supplied by BAK Ambalaj Turkey were produced in their plant in Izmir. They were kindly supplied in form of A4 sized sheets with 30 µm thickness. Methods The functional groups in pearlescent film were determined by infrared (IR spectroscopy). IRPrestige-21 FT-IR 8400S by Shimadzu was used to obtain FTIR spectrum of the film by transmission technique. The DRIFT FTIR spectra of the both surfaces of the film were obtained in Digilab Excalibur FTIR spectrophotometer using Harricks Praying Mantis attachment. Crystal structure of the films were determined by x-ray diffraction using Phillips X’Pert Pro diffractometer

system. Cu Kα radiation was used and a scan rate of 2oθ/min was applied. SEM micrographs of upper and lower surfaces and cross section of gold coated Pearlescent BOPP films were taken by a FEI Quanta 250 FEG type scanning electron microscope. Chemical composition of the film surface was determined by EDX analysis using the same instrument. AFM (Nanoscope IV) and silicon tip was used to obtain surface morphology and roughness of the film. 1 Ohm Silicon tip has coating: front side: none, back side:50 +/- 10nm Al. Cantilever properties are T: 3.6-5.6 µm, L: 140-180 µm, k:12-103 N/m, fo: 330-359 kHz, W: 48-52µm. To achieve surface properties of pearlescent BOPP film, it was cut in 1x1 cm size, then it was put in sample holder in AFM. USRS 99-010, AS 01158-060 serial no OD57C-3930 standard was used in reflection mode. For the reflection spectrum, a black CD was placed at back of the film. Results and Discussion FTIR spectroscopy Figure 1a shows the pearlescent BOPP film FTIR spectrum taken by the transmission method. The peaks between 2950 and 2800 cm-1 correspond to the various aliphatic CH stretching modes. The peaks near 1450 cm-1 and 1380 cm-1 are the CH2 and CH3 deformation bands, respectively [14]. The other peaks below 1400 cm-1 are the well-known “fingerprint” of isotactic PP. The peak at around 1500 cm-1 of pearlescent BOPP film is wide which is caused existence of calcite. The reason of the increase of the peaks around this region is calcite. The bands at ~1420, ~874 and ~712 cm-1 could be attributed to vibrations of CO3 group of calcite [15]. The DRIFT FTIR spectra of the both surfaces of the film are seen in Figure 1b. The peak around 3000 cm-1 for back surface is similar to previous result but for front surface, peak is very small. The spectrum of the surfaces of the pearlescent film was very different from the transmission spectrum, indicating they were made out of a different polymer. PVdC and acrylic coatings were used for making the pearlescent film heat sealable and printable. However without further characterizations it was not possible to identify the polymer surfaces of the film. Fig. 1 - a) DRIFT FTIR spectra of front (dotted line) and back (continious line) surfaces of the film, b) transmission spectrum X-ray diffraction In Figure 2 X-ray difraction diagram of the film in 5-35o 2 thata range is seen. The maximum reflection points of biaxially orientes isotactic polypropylene were observed at 14.2o (110); 17o (040); 18.85 (130); (111) 21.4o; (-131) 21.8o 2 theta values in the figure [16]. Fig. 2 - X-ray diffraction diagram of the film in 5-35 o 2 theta range The sharp peak at 29.4o 2 theta vallue can be attributed to 104 planes of calcite. The X-ray diffraction diagram of the film in 35- 65o 2 theta values is seen in Figure 3. Observed peaks at 36.03, 39.4, 43.2, 47.2, 47.4, 47.6, 48.5o 2theta values are very close to peaks of calcite reported in JCPDS Card Index File, Card 5-5868 [17], which are two theta values of 36.03, 39.4, 43.2, 47.2, 47.5, 48.6. Thus the presence of calcite was also confirmed by x-ray diffraction. Fig. 3 - X-ray diffraction diagram of the film in 35-65 o 2theta range SEM and EDX The SEM micrographs of the cross sections of the film in machine and transverse direction are seen in Figure 4. Fig. 4 - SEM micrograps of the crossections of the film in a) Machine direction, b) Transverse direction The film has a there layer structure. The top and bottom surface

layers which had 4µm thickness dos not have any solid particles. FTIR analysis had indicated that the two surfaces were made out of two different polymers other than the core layer. The SEM micrographs of the surfaces indicated that they were very smooth. The core layer with 22 µm thickness had a stratified structure. There were holes having very high aspect ratio created by the 0.8-3 µm sized particles and the orientation process. The dimensions of the pores in machine direction are length 16.4±6.2 µm and width 0.7±0.3 µm, in transverse direction are length 9.14± 3.99 µm and width 0.47± 0.5 µm. Mean aspect ratios (length/width) of pores observed in Figure 4a and Figure 4b are 23 and 19 respectively. The EDX analysis of the surface of the filler particles indicated that they consisted of Ca, C and O elements. They had a composition similar to CaCO3 which had 40% Ca, 12% C and 48% O. EDX analysis of the particles showed that the particles had 42.8±1.6 % Ca, 22.3±3.73 % C and 34.9 ±5.2 % O. The particles were calcite and they were coated by a compound which was rich in C. AFM study Typical images of the surface of the perleascent film in two and three dimensions are seen in Figure 5. The surface consists of spherical particles. No network stucture was observed as indicated by previous studies for 8:1 draw ratio, indicating the draw ratio of the pearleascent film in machine and transverse direction were close to each other. Fig. 5 - AFM micrographs of the surface of the perleascent films a. Two dimensional b. Three dimensional appearence The surface rougness of the films were determined in three different regions and reported in Table 1. The rootmean square rougness (Rms ) was between 3.052 and 11.261nm and average rougness (Ra) was in the range 2.330-7.326 nm. This low rouhness values indicated that the surface of the pearlescent films was very smooth. Table 1 - Image Statistics of Perleascent BOPP Films at three different regions Scan size, µmx µm 5x5 5x5 1x1 Z range, nm 38.155 113.93 21.031 Raw mean, nm 25.591 53.191 -37.563 Rms (Rq), nm 4.861 11.261 3.052 Ra, nm 3.821 7.326 2.330 Srf. Area, µm² 25.057 25.121 1.003 DSC analysis DSC analysis was used to determine melting point, melting heat and crystallinity, the crystallite size and activation energy of the melting process.The DSC curves of the sample heated at different rates are seen in Figure 6. A shoulder corresponding to the melting of small crystallites was observed at all heating rates. This shoulder was also observed for biaxial oriented polypropylene by previous investigators [18]. The melting temperature shifts to higher temperatures as the rate of heating was increased. Table 2 shows enthalpy of melting, melting temperature and crystallinity determined at different rates of heating of the film. The degree of crystallinity (Xc) of the samples from DSC melting peaks were determined using Equation 1. (1) Where ΔHm is the melting enthalpy of the samples (J/g) and ΔH0f is the heat of the fusion of PP at 100% crystallinity, correspondent to 207 J.g-1[18]. The crystallinity of the film also increses with the rate of heating. Table 2 - Enthalpy of melting, melting temperature and crystallinity determined by DSC B, oC/min ΔHm, J/g Tm, oC Crystallinity, % Lc ,nm 5 87.63 162.9 48 6.1 10 93.75 163.6 51 6.3 15 129.07 164.2 60 6.5 The Thompson-Gibbs equation predicts a linear relationship between Tm

and the reciprocal of crystal thickness. (2) Where σ is the fold surface free energy, T0m is the equilibrium melting temperature, ρc is the crystal phase densitiy of pp, ΔH0f is the heat of the fusion of PP at 100% crystallinity, correspondent to 207 J.g-1[19], and Lc is the thickness of the lamellar crystals. T0m is 459,1 K [20], ρc is 946 kg/m3 [21] and σ is 30.1 mN/m [22]. The crystal thickness values determined by using the melting temperature for different heating rates are reported in Table 2. They were in the range of 6.1 to 6.5 nm. Fig. 6 - DSC curves of the film at 1. 5oC/min, 2.10oC/min, 3. 15oC/min heating rates Conclusion A pearlescent packing material supplied by BAK ambalaj Turkey was characterized for obtaining information about its properties for its application fields and its recycle in industry. The advanced characterization techniques such as FTIR spectroscopy, x-ray diffraction, SEM, EDX, AFM and DSC were used for this purpose. The bulk film was polypropylene and it was biaxially oriented as shown by FTIR spectroscopy and X-ray diffraction respectively. FTIR spectroscopy indicated presence of carbonate ions, the presence of Ca element was indicated by EDX analysis. X-ray diffraction showed the presence of calcite. The 30 μm film consisted of a core layer of polypropylene filled with calcite and 4 μm thick upper and lower layers without any filler were from different polymers. There were long air cavities in the core layer with aspect ratios of 23 and 19 in machine and transverse directions making the film pearlescent. The surfaces of the film were very smooth and had a surface rougness in the range of 3.052 and 11.261 nm as determined by AFM. The film melted at 163.6 oC had 51 % crystallinity and had 6.3 nm polymer crystals for 10 10 oC/min heating rate.