

Introduction 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 [1]. 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 [2, 3]. 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 [4]. The aim of the present study is characterization of a commercial pearlescent BOPP film by advanced analytical techniques. The light transmission and reflection, melting and thermal degradation of the film and mechanical properties 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 film was thermally treated under pressure to eliminate its pores. Thus the transparency of perlescent film and heat treated film were tested. The perlecent film's thickness was reduced from 30 μm to nearly 23 μm by in a compression molding machine (Shinto) in two stage. Film is exposed in the hot press with pre-heated for 3 minutes under 0 kg/cm² pressure, then heated for 3 minutes at 60 kg/cm². After this stage, film was placed in a cold press for 3 minutes at 150 kg/cm². The light transmission from the films were tested by covering the surface of a paper with our Institute's logo. The stress strain diagrams of the film in machine direction and transverse direction were obtained with Texture Analyser TA-XT2 (Stable microsystem, Godalming, UK) having Exponent stable Micro Sytem software. The test is done in ASTM D882. The strips with 5 mm width and 10 mm length were strained with 5 mm/min rate.

Results and Discussion TG analysis Thermo gravimetric analysis (TGA) method was also employed to understand thermal degradation behavior of the BOPP film. Typical weight loss (TGA) curves of BOPP film at heating rate 5, 10 and 15 oC/min under nitrogen is seen in Figure 1. It is observed that thermal degradation process of BOPP film proceeds in two stages. The first stage corresponds in to the degradation of polymer. The second stage is related to the decomposition of calcium carbonate. The degradation of the BOPP film started at 235 oC, 258 oC and 265 oC at heating rate of 5 oC, 10 oC and 15 oC/min respectively. The maximum rate of degradation of BOPP film was 358, 404.6 and 412 oC at 5 oC, 10 oC and 15 oC/min heating rates respectively. The second step of the mass loss observed in Figure 1 was for the decomposition of calcite. Figure 1 display that the degradation of the calcium carbonate started at 648 oC, 670 oC and 675 oC at the heating rate 5, 10 and 15 oC/min and its rate was maximum at 690 oC, 721.5 oC and 714.7 oC. for 5 oC, 10 oC, 15 oC heating rates.

Fig. 1 - TG curves of the film for 1. 5 oC/min, 2.10oC/min, 3.15

oC/min heating rates The second stage of the mass loss belongs to decomposition of calcium carbonate. The calcium carbonate decomposes calcium carbonate and carbon dioxide; $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ (1) If one mole of calcium carbonate decomposes, one mole of calcium oxide and one mole of carbon dioxide would form. Thus the second step is for the evolution of CO_2 from CaCO_3 . From the mass loss of the second step of the degradation curve it was found that the film contained 11.2 % CaCO_3 . In this study decomposition activation energy was determined by using Flynn and Wall equation. Flynn and Wall is derived a convenient method to determine the activation energy from weight loss curves measured at several heating rates. The following relationship is used to calculate the activation energy [5]. (2) where E - activation energy (J/mol), R - gas constant (8.314 J/mol K) and b constant (0.457) [5]. The values of 1, 2 and 5 % decomposition level were chosen to determine the activation energy for degradation of the polypropylene and temperatures for these conversions were read from Figure 1. The activation energy was determined directly by plotting the logarithm of the heating rate versus $1000/T$ at constant conversion. The plotted data produced straight lines with R^2 values higher than 0.93. From the slopes the activation energy values were found and they are reported in Table 1. The average activation energy was 64.8 kJ/mol. Table 1 - Activation energy for degradation of polypropylene and calcite

	Polypropylene	Calcite
Mass loss, %	1	2
R^2 value	0.99	0.96
E_a , kJ/mol	64.8	66.4
Mass loss, %	5	5
R^2 value	0.93	0.99
E_a , kJ/mol	63.4	209.1

The activation energy for the decomposition of the calcite in the film was determined in the same manner and reported in Table 1. The average activation energy for the decomposition of calcite was found as 204.8 kJ/mol. Optical properties The unique luster of pearls depends upon the reflection, refraction, and diffraction of light from the translucent layers. The thinner and more numerous the layers in the pearl, the finer the luster. The iridescence that pearls display is caused by the overlapping of successive layers, which breaks up light falling on the surface [6]. Polypropylene polymer can reflect only a very small percentage of incoming light. Using Fresnel equation: (3) In the above equation, ' n_1 ' and ' n_2 ' indicate the reflection indices of polypropylene and air, respectively. Reflection values were calculated considering Fresnel's equation. Reflection index of polypropylene is 1.49 and 1.0 for air [7]. Then, reflection (R, %) was calculated as 3.87%. However the film under study reflects 85% of light at 400 nm and 65% at 700 nm as seen in its reflection spectrum in Figure 2. The thin layers and the air gaps between them is the cause of this pearlescent effect. Fig. 2 - Reflection spectrum of the film under study It was reported that BOPP films were transparent to light and the their smoother surface they had, the more transparent they were [8]. It followed that the clearest films were obtained from sheets with the most homogeneous texture, such as obtained by quenching from the melt, and by orienting at the lowest temperature, which minimized the amount of melting [8]. The film in the present study was a sandwich type BOPP film having a core layer with calcite. The film reflects light but it does not transmit it. The transmission spectrum of

the film is shown in Figure 3. Fig. 3 - Transmission spectrum of the film in visible region It indicated that 0.36 % of incident light was transmitted at 400 nm and 0.5 % was transmitted at 700 nm. The light was not transmitted from the film because of the air holes in the film. When these holes were removed by hot pressing the film, it became transparent as seen in Figure 4. The logo of our Institute covered by the pressed film was visible, but when the logo was covered by the pearlescent film it was not visible. The pearlescent film was opaque and when the air holes were removed it was transparent even if it contained 12 % calcite. It was the air gaps not the calcite making the film opaque and pearlescent. Fig. 4 - a) Paper surface without sample films, b) paper surface covered with sample films: left side was covered with nearly 23 micron film pressed film, right side was covered with 30 micron original white BOPP film

sample Mechanical Properties The mechanical properties of BOPP in machine and transverse direction are different. In Figure 5 and Figure 6 stress strain diagrams of the film in transverse and machine directions are seen. The tensile strength in transverse direction is lower and strain at break is higher than those of machine direction as reported in Table 2. Tensile stress 35.9 MPa and 97.7MPa , elongation at break 157 % and 37 % for transverse and machine directions respectively. No yield point was observed in the BOPP film with calcite. BOPP film without calcite was characterized by Yuksekkalayci et al [9] and it had the yield point (34.2 MPa and 42.2 Mpa) machine direction and transverse direction. The film without calcite had higher values of tensile stress (151 MPa and 270 MPa) [9] in machine and transverse directions than the film with calcite. However the elongation at break values (150 %, 32 %) were closed to the values for the film with calcite. The presence of pores lowers the tensile strength, however the elongation values were closer. The modulus of elasticity of the film under study also changed with direction. It was lower (0.129 MPa/%) in transverse direction than in machine direction (2.93 MPa/%). However the film without calcite had much higher elastic modulus values 2.8 to 5.9 GPa. Thus the calcite filled BOPP film was much more flexible than the film without calcite. Fig. 5 - Stress strain curve of the film in transverse direction Fig. 6 - Strain stress diagram of the film in machine direction

Table 2 - Mechanical properties of the film in machine and transverse directions

Direction	Stress, MPa	Strain, %	Young Modulus, MPa/ %
Transverse	35.9 ± 11.62	157.7 ± 31	0.129 ± 0.065
Machine	97.2 ± 20.6	37 ± 7.7	2.93 ± 0.51

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 TG analysis, visible spectroscopy and tensile testing were used for this purpose. The bulk film was polypropylene and it was biaxially oriented. Thermal gravimetric analysis indicated 11.2 % of calcite in the film. The film thermally degraded in two steps. The first step was for the polymer fraction and the second step was for decomposition of calcite. For 10oC/min heating rate the onset of polypropylene degradation was 250 oC and calcite decomposition was 670 oC. The activation energies for polypropylene degradation and

calcite decomposition were 64.8 kJ/mol and 204.8 kJ/mol. The film reflected but not transmitted visible light. The tensile strength of the film in machine and transverse directions were different and it was 97.7 and 35.9 MPa respectively.