Characterization of Biaxially Oriented Polypropylene Films by Atomic Force Microscopy and Microthermal Analysis

M. J. ABAD, A. ARES, L. BARRAL, J. CANO, F. J. DÍEZ, J. LÓPEZ, C. RAMÍREZ

Departamento de Física, E. U. P. Ferrol, Universidad de A Coruña. Avda 19 de Febrero s/n, 15405 Ferrol, Spain

Received 11 July 2001; accepted 14 November 2001

ABSTRACT: A new method for evaluating the thermal properties of the films and detecting fabrication failures has been provided. Moreover, this article studies the characterization of biaxially oriented polypropylene films (BOPP) using the Microthermal Analizer (μTA 2990). This instrument combines high-resolution imaging capabilities of the atomic force microscopy (AFM) with physical characterization by thermal analysis. In the first part of the work, topographic images of the film surfaces were obtained by AFM. They showed that the fabrication process and additives to the films caused differences in the sample topography. In the second part, the thermal conductivity images of multilayer films were obtained by thermal analysis mode. The thickness of each layer was determined for several BOPP films, based on the thermal conductivity signal registered by μTA 2990. Finally, it has been proven that this new technique is valid for detection of thermal transitions in polymer samples. Thus, melting points and glass transitions were measured in the samples with thermal probe.
 J Appl Polym Sci 85: 1553–1561, 2002

Key words: atomic force microscopy; polypropylene films; thermal properties

INTRODUCTION

Biaxially oriented polypropylene (BOPP) film has been a widely used packaging material since it was introduced to the industry in the 1960s. There are two basic techniques for the production of BOPP films: tubular process or tenter process. In this article, the BOPP films used are multilayer films that have been coextruded, using a twin-screw extruder, by the tenter process. In this fabrication process, the polypropylene pellets are extruded through a flat die as a sheet that is cooled under controlled conditions. The cool sheet called cast film is reheated to orient it. First, the film passes over a system of rolls running at different speeds, which oriented it in the "Machine Direction (MD)." Subsequently, the film is enclosed in a hot air oven and oriented in the "Transverse Direction (TD)" by a system of chain-mounted clips that stretched it. Upon emerging from the oven the film is pretreated and the edges are removed. Finally, the film is wound up and stored. This process is used to obtain films with different commercial and technical properties.[1]

AFM[2] is a technique that can detect the variation in height or topography of a sample surface. The advantage of AFM over other techniques [like scanning electron microscopy (SEM) or transmission electron microscopy (TEM)] is that extensive sample preparation, such as staining or metal coating, is not required. In the contact mode AFM

Correspondence to: L. Barral (labpolim@udc.es).
Contract grant sponsor: Xunta de Galicia; contract grant number: XUGA-PGIDT00PXI172018R.

Journal of Applied Polymer Science, Vol. 85, 1553–1561 (2002)

method, the probe scans the surface and maintains a constant force over it. The voltage required to raise and lower the probe (maintaining the constant force) is directly related to the surface topography. AFM, until recently, has been used only to obtain images of surfaces.

The development of scanning thermal microscopy (SThM) has allowed researchers to evaluate the microscale thermal properties of materials. In the 1990s, recent innovations combined the high spatial resolution of AFM with the characterization capabilities of thermal analysis. This approach was called "microthermal analysis." The thermal imaging inclusion in AFM systems was realized by Dinwiddie et al.[3] and Pylkky et al.,[4] followed by Price et al.,[5] among others.

The aim of this article is to show the power of the new techniques (like the AFM and the microthermal analysis) in the characterization of BOPP films. On the one hand, the surfaces of the films with different characteristics were studied by AFM. And on the other, the microthermal analysis was used to measure the thickness of its layers and other thermal properties.

EXPERIMENTAL

The instrument used was a Microthermal analizer μTA 2990 (TA Instruments). It can work in two operating modes: Atomic Force Microscopy (AFM) and Thermal Analysis mode.

To obtain an image of the sample surface by AFM, a cantilevered probe is positioned at the area of interest brought into contact with the surface, and a constant force between the sample and the probe is maintained. Two piezoelectric elements control the motion of the probe in the x and y axis. The height of the sample is measured by the deflection of a laser beam that is focussed in back of the probe and is reflected in a split photodetector. A z-axis piezo controlled by a feedback loop moves up and down to maintain a constant force on the sample.

The thermal analysis of the samples is realized using a V-shaped platinum thermocouple probe that works as a temperature sensor and as a topography sensor (similar to conventional AFM cantilever probes but with worse resolution). The thermal probes can image the sample surface utilizing the piezoelectric feedback of the AFM. Several images of the sample can be generated with the thermal probe: topographic image, thermal conductivity image, and if the temperature is modulated, the AC thermal image. The latter is connected with the thermal diffusivity of the sample.

These probes can realize local thermal analysis (LTA) and measure thermal properties. The probe is placed at a point on the sample surface. The AC current passes through it, and heats the probe following the programmed ramp. In the LTA, μTA 2990 records two signals at the same time. The z-axis movement of the probe or sensor signal is monitored as a function of the temperature. It is called microthermomechanical analysis (μTMA) because it represents the microscopic equivalent to the thermomechanical analysis (TMA). With the probe position signal, thermal events like glass transitions and melting points can be recognized. Moreover, the instrument measures the difference between the power required to make the probe follow the temperature program and the power supplied to a reference probe isolated at room temperature. The curve of the differential power vs. temperature gives calorimetric information about the nature of measured transitions. This signal is equivalent to the conventional modulated DSC curve, although the obtained information is more qualitative than quantitative.[6]

Calibrating the μTA 2990

The μTA 2990 has several calibrating routines: the scanner calibration, the temperature calibration, and an electronic calibration called I/O-T Offset. Except for the scanner calibration, the other ones must be performed at least daily, and always when the probe is changed.

The scanner calibration is checked with a test grid. An area of 20×20 μm is scanned with the AFM probe. The rate used was 20 μm/s. Figure 1(a) shows an area of the test grid with a pitch size of 3.0 μm. Once the test grid has been imaged, a line in the image was chosen and at least the size of five pitches was measured. The mean value of the measured features was calculated and compared with the real size of the test grid pitch [see Fig. 1(b)]. If a significative error is found (higher 2%), the scanner should be calibrated. For that, the instrument software has an active window that allows correction of the error in the calibration. After the scanner has been

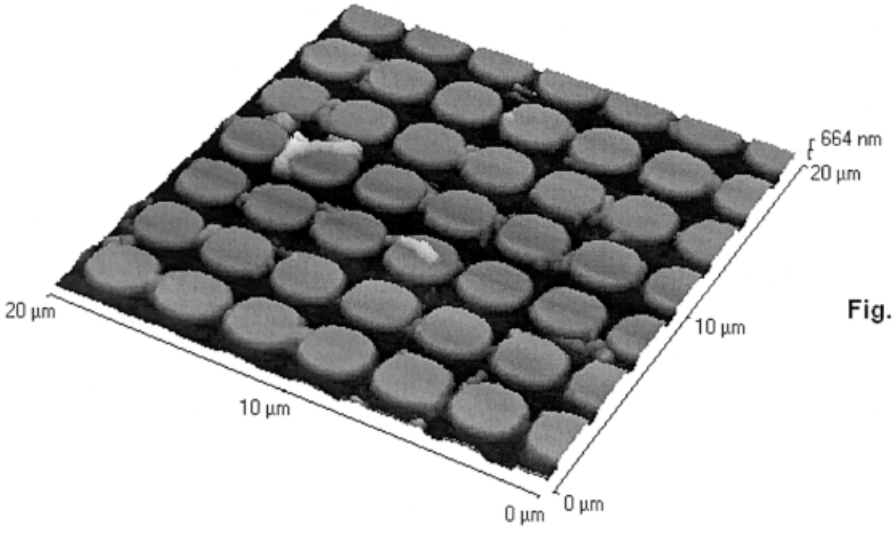


Fig. 1a

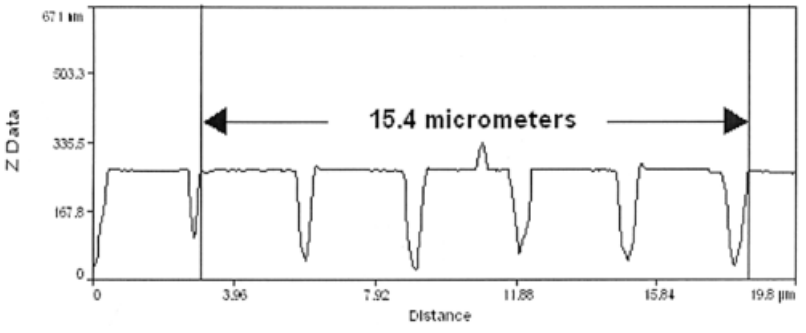


Fig. 1b

Figure 1 (a) Topographic image in 3D of test grid by AFM. (b) Measurement of the pitch length.

recalibrated, a new experiment is performed to confirm that the calibration is correct. The scanner calibration is periodically checked and corrected if it is necessary.

The temperature calibration needs that the I/O-T Offset calibration has been checked before. This electronic calibration compensates for the small hysteresis in the temperature control electronics. To calibrate, the "I/O-T Offset calibration window" should be selected from the software menus and an automatic routine is performed by the instrument software. To check the temperature calibration, a polyethylene terephthalate (PET) sample was used, which is a standard certified material with known melting temperature (244.9 ± 0.1°C). After the topographic image of the PET surface is obtained with the thermal probe, a point was selected in the sample and a LTA was realized at that point. The probe was heated from 120 to 300°C at 10°C/s and then cooled at the same rate. A frequency of 5 kHz and an amplitude of 10°C were the parameters of the temperature modulation. The probe position signal and the power signal were registered and represented in the Figure 2. The solid line corresponds to the sensor signal and the dashed line, to the power signal.

As the μTA 2990 cannot work below room temperature, the temperatures smaller than the room temperature are not real. When the probe

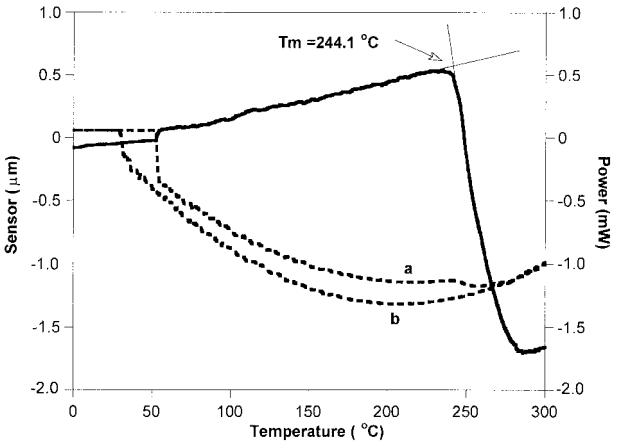


Figure 2 Local thermal analysis on the melting temperature of PET. Sensor signal (solid line) and power signal(dashed line), heating curve (a) and cooling curve (b).

reaches the room temperature (heating or cooling) a step appears in the power signal. This point selected in the cooling curve (curve b in Fig. 2), is a calibrate point. The second calibrate point is the PET melting point measured like an onset in the power signal or in the probe position signal. The instrument software measures the probe resistance in the two calibrate points and fits a calibration line that allows the probe temperature as function of its resistance to be known. A new LTA is necessary to check that the calibration is right. Moon et al.[7] have shown that the μTA 2990 can reach a temperature precision about ± 3 K if a good calibration is realized.

Materials

The extrusion grade of polypropylene was synthesized by Exxon Mobil™, Chemical Polymères SNC, Notre Dame de Gravenchon, France. Its melt flow index value is of 3 g/10 min. The films were made by Polipropileno de Galicia, S.A. (POLIGAL), Ferrol, Spain.

These coextruded films have three layers: a polypropylene central layer and two external layers, which are composed of an ethylene–propylene copolymer. Films with different thickness were studied.

Sample Preparation

To see the film surface, the sample did not need any special preparation. A bit of film was cut and placed on the sample holder with a double side tape. Then the surface was scanned to obtain the topographic image by AFM mode.

As the BOPP films have three layers, we tried to measure the thickness of each one, by microthermal analysis. For this, it was necessary to embed a strip of the polymer film into a rigid support made of an epoxy resin, enabling a cross section to be made. The resin was cured at low temperature, to prevent the heat released by the exothermic reaction from damaging the film. The curing schedule was 24 h at 4°C. Immediately after, the samples were cut with a microtome Microm GmbH type HM 350 S, with a tungsten carbide knife. A surface with a roughness smaller than 10 μm was obtained and scanned with a thermal probe.

Imaging the Samples

The AFM pictures have been scanned in an area of 100×100 μm, with 400 resolution pixels. The scan rate was 100 μm/s. However, it was sometimes necessary to made a zoom of the interest area in the topographic images. To measure the thickness of film layers the samples were scanned with a thermal probe. The thermal conductivity and topographic images were recorded, with the same parameters than the AFM pictures (that is, area of 100×100 μm, 400 resolution pixels, and scan rate of 100 μm/s). The thermal probe was maintained at 100°C to observe the thermal conductivity differences between the film and the resin. After the conductivity image was obtained, this one was used to select the points where the thermal properties were measured by a local thermal analysis (LTA). In this way the probe was placed in the selected points and the thermal ramp was realized with a rate of 10°C/s, a frequency of 5 kHz and an amplitude of 10°C.

RESULTS AND DISCUSSION

Figure 3(a) and 3(b) show the surfaces by AFM of a metallic BOPP film. The differences in the topographic images between the metallic and nonmetallic faces are observed. To metallize the films, the aluminium is ionized on vacuum and then the ions are placed on the film surface. In this way, it is made a thin layer of aluminium.

In Figure 3(a), the scale shows the highest position reached by the probe when the area is

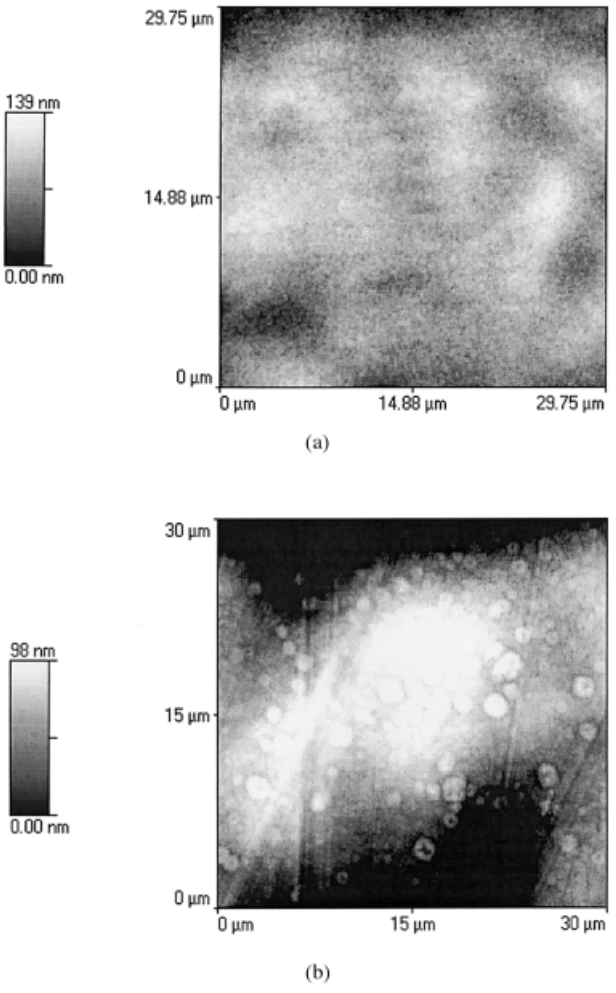


Figure 3 Topographic image of a metallic film by AFM. (a) Metallic face and (b) nonmetallic face.

scanned. The topographic image shows that the metallization is not regular over all the film surface. The nonmetallic surface has a lower roughness than the metallic one [Fig. 3(b)]. The small marks that can be seen in the nonmetallic face are caused by the film fabrication. When the film is cooled, one of the faces is kept in contact with a chill roll and the other one is cooled in a water bath. This last one corresponds to the nonmetallic face and its characteristic appearance is due to the cooling process.

Figure 4 displays the surface of a pearly BOPP film. To obtain the characteristic color of the pearly film, calcium carbonate is added to polypropylene. The protuberances that are seen in the picture are caused by the decomposition of this additive in its fabrication. This topographic image shows if $CaCO_3$ is uniformly distributed or not, and whether there are failures in the fabrication process. This information is very useful for the quality control of the film.

The cross sections of BOPP films with different thickness were studied in the second part of the work. Figure 5(a) and (b) show the thermal conductivity images of two films obtained by microthermal analysis. The film is clearly observed inserted into the resin support. The film and the resin are distinguished due to the differences in their conductivity values. The greatest values (the light gray points) correspond to the film, whereas the lowest ones (the dark gray points), to the resin.

To distinguish between the lateral layers and the central layer was difficult. The last ones can be seldom identified in the thermal conductivity images. It is not easy to measure the lateral layers of the films because their thermal conductivity values are nearly the same, and the thickness of the external layer is about several micrometers close to the spatial resolution of the instrument when it works with the thermal probes.[7]

In general, it was not possible to do a direct measurement of the external layers with the μTA2990. The graphic of the Figure 6 shows the thermal conductivity data vs. the distance belong to the sketched line in the Figure 5(a). The software makes possible to measure lengths in these graphics. Despite the noise, a jump can be seen in the signal corresponding to the thermal conductivity of the central layer. This allowed one to measure the thickness of the homopolymer layer. At least three measurements were performed at different places

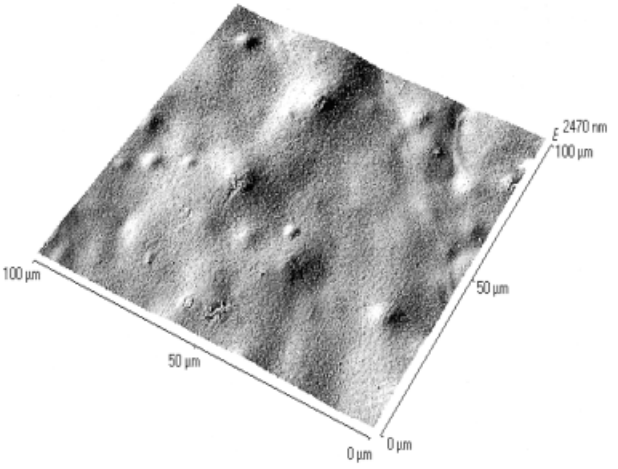
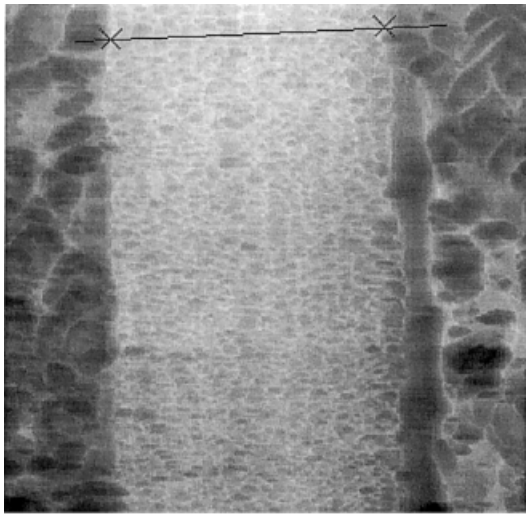
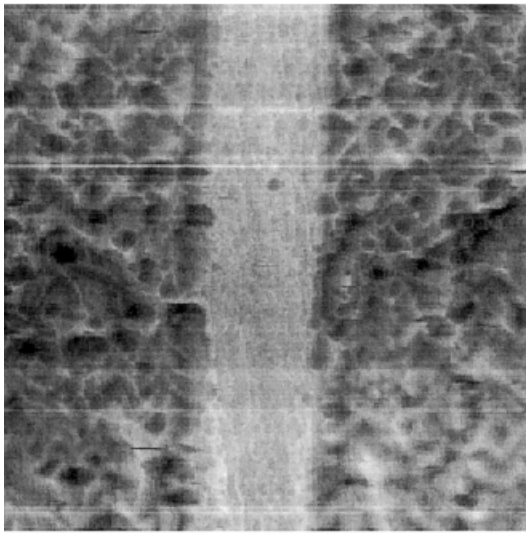


Figure 4 Topographic image in 3D of a pearly film surface.



(a)



(b)

Figure 5 Thermal conductivity image of a BOPP film cross section. The films have a thickness of 60 (a) and 25 μm (b).

of each sample to obtain the mean value of its thickness. Knowing this value and the total thickness of the film that was measured with a micrometer, the thickness of the external layers was calculated for different films. Table I summarizes the mean values and the standard deviations of all data. The low percentage errors in the measurements of the central layer showed that the layers are quite regular. In this way the distribution of thickness between the central layer and the lateral layers are nearly constant also. This one is important to show that the film properties are always the same and with the same economic cost.

In addition, local thermal analysis (LTA) was realized on the sample. The thermal probe was placed on the homopolymer layer and heated from 0 to 350°C at 10°C/s. The sensor signal is showed in the Figure 7. When the probe reaches the melting temperature of the sample the material is softened and the probe goes into it. The instrument records a drop in the sensor signal. The onset of the curve corresponds to the melting temperature of the polypropylene (169.8°C). This value agrees with the melting point obtained by the calorimeter. DSC measures thermal transitions of several milligram samples, whereas μTA 2990 measures transitions in a spot (over a micron cubic of material).[8] Because of this, the values are not exactly comparable.

Furthermore, the μTA2990 measured the small step in the power supplied to the probe when this one reached the melting point of the polypropylene. This power change is connected with the power absorbed by the sample to effect the transition, although the information obtained in this signal is quantitative in temperature but qualitative in calorimetric measurement.

Lastly, a LTA was performed on the resin. The temperature conditions were exactly the same as the other experiment. The sensor signal vs. the temperature is represented in the Figure 8. The resin's response to the thermal ramp is characterized by a step change in the sensor signal that corresponds to the glass transition of the specimen.[9] In the curve, the thermal expansion of the sample when the probe temperature raises can also be observed. The μTA2990 is not able to register any noticeable change in the power required to heat the probe because the power

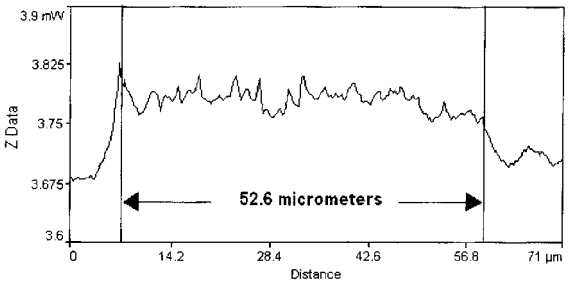


Figure 6 The thermal conductivity values as a function of the distance. The graph corresponds to the line sketched in Figure 5 (a).

Table I Thickness values of the BOPP film layers

Film Thickness (μm)	15	25	40	50	60
	13.6	22.6	36.1	44.4	52.3
Central layer thickness (μm)	13.4	23.0	36.0	44.1	52.2
	13.0	22.8	35.8	45.2	53.2
Mean	13.3	22.8	36.0	44.0	52.6
Deviation	0.3	0.2	0.1	0.6	0.5
Lateral layers thickness (μm)	1.7	2.2	4.0	5.4	7.4

change in the glass transition is too low. Tillman et al.[10] found out that the microthermal analysis has limitations to evaluate the glass transitions of thermosetting materials. They discovered that the transition reproducibility depends the molecular size of the polymer and the experimental ramp rate. Sometimes the instrument is not able to detect changes in the power signal when the probe temperature reach the T_g.

CONCLUSIONS

In this article, the characterization of BOPP films has been described. The μTA2990 seemed like a

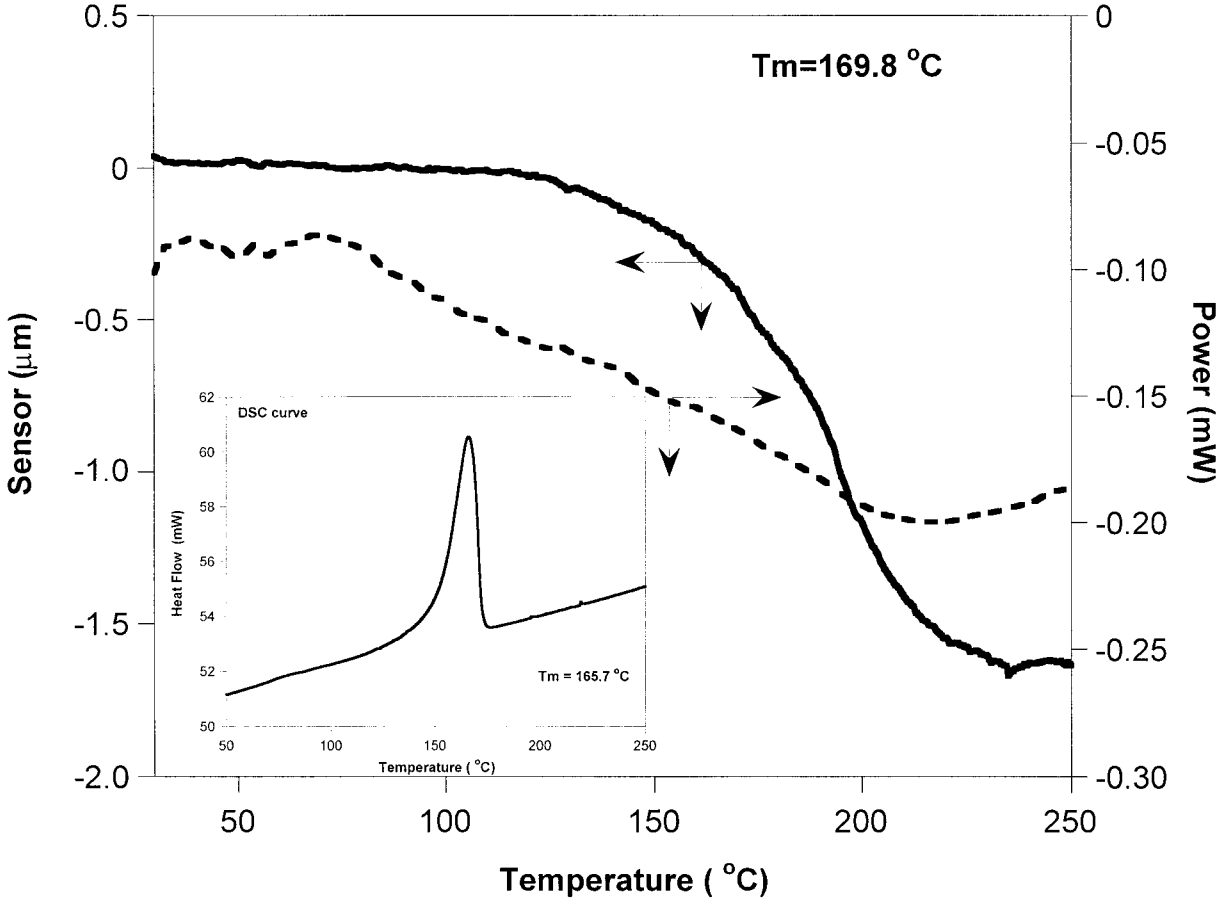


Figure 7 Local thermal analysis on the melting temperature of the homopolymer layer. Sensor signal (solid line) and power signal (dashed line). The zoom shows the melting transition measured in the DSC.

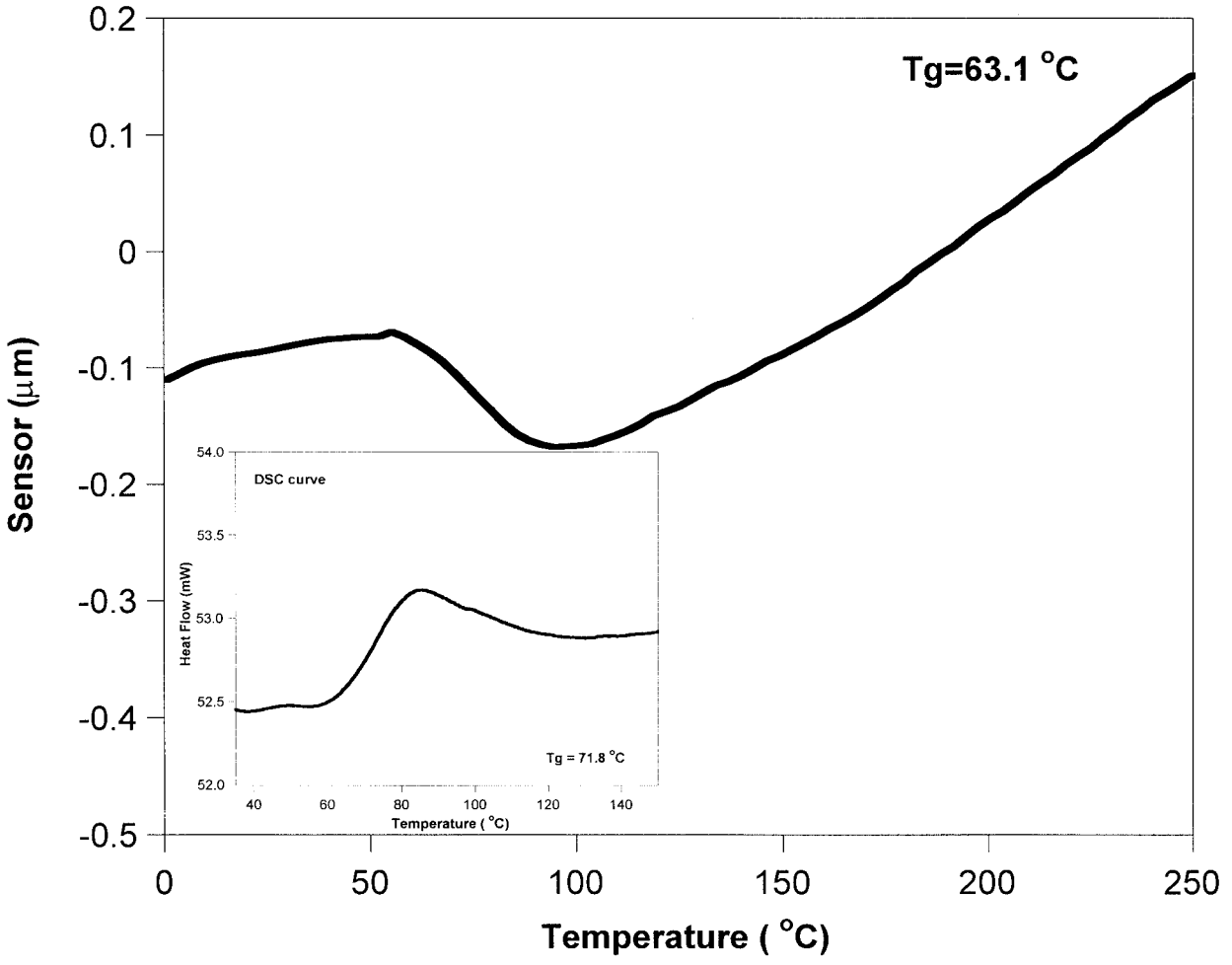


Figure 8 Sensor signal as function of the temperature on T_g of the resin. The zoom displays the DSC curve and the glass transition temperature of the resin measured in the calorimeter.

new instrument with a lot of applications in polymer science.

The higher resolution probe for AFM mode obtains a good image definition to nanometer scale resolution. This allowed one to study the surfaces of different films. In the AFM images of the metallic film, the roughness differences between the metallic side and nonmetallic side have been seen. The pearly film exhibits a characteristic surface in the AFM images due to the $CaCO_3$ added during the fabrication process. With this technique, fabrication failures can be detected in the films, realizing a fast and nondestructive experiment.

In the second part of the article, we tried to measure the thickness of the film layers by microthermal analysis. The thermal conductivity images were used to distinguish between the film and the resin support. The thermal conductivity values allowed measuring of the thickness of the central layer. Starting on that data, the thickness of the lateral layers were calculated.

The microthermal analizer is also a useful tool for measuring variances in thermal transitions throughout a sample where traditional techniques (like DSC) are not available.

The melting points of the central layer of the films were measured with the thermal probe. In the same way, the glass transition temperature of the resin was obtained. The values correlated well to similar experiments performed using DSC, although the data are not the same because the measuring techniques are different.

Support for this research was provided by Xunta de Galicia (XUGA-PGIDT00PXI172018R). The authors would like to thank Polipropileno de Galicia, S. A. (POLIGAL), Ferrol, Spain, for the preparation of BOPP films.

REFERENCES

1. Yuksekkalayci, C.; Yilmazer, U.; Orbey, N. Polym Eng Sci 1999, 39, 1216.
2. Smith, D. P. E.; Binnig, G.; Quate, C. F. Appl Phys Lett 1986, 49, 1166.
3. Dinwiddie, R. B.; Pylkki, R.; West, P. E. Therm Conduct 1994, 22, 668.
4. Pylkki, R. J.; Moyer, P. J.; West, P. E. Jpn J Appl Phys Part 1 1994, 33, 3785.
5. Lever, T. J.; Price, D. M. Am Lab 1998, 30, 15.
6. Price, D. M.; Reading, M.; Hammiche, A. Pollock, H. M. J Therm Anal Calorim 2000, 60, 723.
7. Moon, I.; Androsch, R.; Chen. W.; Wunderlich, B. J Therm Anal Calorim 2000, 59, 187.
8. Hammiche, A.; Reading, M.; Pollock, H. M.; Song, M.; Hourston, D. J. Rev Sci Instrum 1996, 67, 4268.
9. Tillman, M. S.; Hayes, B. S.; Seferis, J. C. J Appl Polym Sci 2000, 80, 1643.
10. Tillman, M. S.; Takatoya, T.; Hayes, B. S.; Seferis, J. C. J Therm Anal Calorim 2000, 62, 599.