

Optical Expandometry: A Technique to Analyze the Expansion Kinetics of Chemically Blown Thermoplastic Foams

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ABSTRACT: A novel technique to determine *in situ* the free expansion kinetics of chemically foamed thermoplastic foams, so-called optical expandometry, is presented in this work. This technique is based on the camera monitoring of a free-foaming material placed inside a furnace. Images are acquired under special illumination conditions to facilitate the later image processing. The present article explains the experimental set-up and the image processing methods used to determine the free volumetric expansion of different polyolefin-

based foams. The results are compared with those obtained using thermo-mechanical analysis. In addition, several possible applications of this method are detailed, such as studying the effect of polymer rheology, foaming temperature, blowing agent content and the anisotropy of the expansion. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1059–1067, 2012

Key words: thermoplastics; foams; kinetics; foamability; expandometry

INTRODUCTION

Nowadays, there is an increasing demand for the development of lightweight materials with tailor-made properties. The extension of the specific properties range due to density modification, the reduction in raw materials and thus costs, as well as the possibility of adding specific characteristics through both cellular structure control, and incorporation of functional fillers easily explain the great interest and promising future of polymer foams in sectors such as the automotive, aeronautical, renewable energies, construction, cushioning and packaging, biotechnology, among many others. However, there is still a lack of knowledge concerning some scientific and technological aspects of these materi-

als, limiting the development of new products. Particularly, the understanding of the foaming behavior of polymer-based systems is a field in which further research is still required.

Foaming is a phenomenon where many physical and chemical mechanisms occur simultaneously.^{1–3} Cell nucleation and growth, pore coarsening mainly due to cell coalescence and possible drainage observed in some materials, play a key role during foaming. Frequently, *ex-situ* techniques, in which the density and cellular structure of the foam are analyzed after foaming, have been considered to analyze these effects.^{4–6} In these studies, the evolution of the material during foaming is usually not recorded, making more difficult to perform a proper analysis of the involved mechanisms and foamability of a given formulation at specific foaming parameters (temperature, time, etc.).

Due to this reason, some developments regarding the *in situ* analysis of the foaming behavior have appeared over the years. Different experimental challenges have to be considered depending on the type of polymer base material. In the case of thermosets, usually foamed at room temperature and atmospheric pressure, the experimental set-up is commonly simpler than that required for thermoplastics, usually foamed at temperatures above the glass transition (amorphous polymers) or the melting temperature (semicrystalline polymers) of the

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base polymer and in several cases under pressure. Due to the significant market for thermosets,⁷ there are several research works dealing with the *in situ* analysis of the foaming behavior of thermoset foams. For instance, several methods have been used to study polyurethane foams. These include floats placed in the foam's surface,⁸ recording the foam height by simply using rulers,⁹ or optical devices.^{10,11} By far the most elegant method is based on the measurement of the buoyancy force exerted by air during expansion.¹²

In the case of thermoplastic materials, it is necessary to differentiate between foams produced at atmospheric pressure and those produced under high pressure conditions. In the last few years, some articles have been published proposing experimental set-ups for the analysis of cell nucleation in foams obtained in high-pressure autoclaves through a gas dissolution process followed by sudden pressure drop and rapid cooling (pressure-quenching).^{13,14} On the other hand, the foamability of thermoplastics chemically foamed at atmospheric pressure has been assessed using thermo-mechanical analysis (TMA),^{15,16} although in these tests foaming was carried out inside a mold to avoid radial expansion, which could affect the measured expansion (see comparison between optical and mechanical techniques in the Results and Discussion section for further discussion on this effect).

Aluminum foams produced via the powder metallurgical route¹⁷ are, by far, the materials that have been more intensively studied using these *in situ* techniques. The term expandometry was actually used for the first time when addressing this kind of characterization technique for these materials. Particularly, their foaming mechanisms and expansion behavior have been deeply studied during the last 10 years by *in situ* techniques considering the necessity that researchers had on finding potential foaming alloys and understanding the stabilization mechanisms. Initially, mechanical expandometers similar to thermo-mechanical analyzers were used.¹⁸ Later on, these devices were replaced by optical contactless systems. Among others we can cite the laser beam expandometer¹⁹ or optical expandometers with coupled image analysis.²⁰ In parallel, X-ray radiography was identified as a promising technique, with the advantage of monitoring the internal evolution of the cellular structure, successful results being obtained using synchrotron radiography.²¹ In the last couple of years, the resolution of X-ray synchrotron radiography has been greatly improved, reaching ultrahigh time and spatial resolutions and providing some new data on aluminum foams.²² Finally, we can mention that X-ray lab facilities have been built in the last years with the objective of providing a deeper knowledge of these metallic cellular materials.²³

There are several possible applications of the *in situ* techniques to the study of the foaming behavior of polymer-based materials.

Expansion kinetics: It helps to determine the characteristic expansion rate and its onset temperature for different polymer-based foaming formulations. Considering that many polymeric foamed systems contain a thermally-activated decomposing chemical blowing agent, the expansion behavior is expected to depend on the heating rate, maximum temperature, and blowing agent content.²⁴

Maximum expansion: The material will reach a maximum expansion that will depend on the heating rate, blowing agent content, and polymer rheology during foaming. Although these materials may be later foamed using different processes, such as compression-molding, direct extrusion, etc., these tests may give an idea of the maximum expansion and the required heating rates to obtain the lowest possible densities for a given formulation.

Collapse/stability kinetics: After reaching the maximum expansion, if the sample is maintained at a constant temperature, it will eventually collapse. The inner rheological nature of the base polymer or composite, additionally influenced by crosslinking, grafting or by secondary inorganic phases, may allow the material to reach a higher expansion and/or a slower foam decay by limiting cell coalescence and gas loss.²⁵

In addition, for several processing methods it is important to study the possible anisotropic expansion of precursor materials and the eventual influence of previous blending/processing conditions and/or polymer thermal treatments. As it is demonstrated in this work, under certain processing conditions it was possible to observe significant direction-dependent expansions.

Bearing the previous ideas in mind, this work is focused on establishing a better and simpler technique than the existing ones, such as TMA, to follow up the free expansion of chemically foamed thermoplastics. Particularly, it introduces a testing method based on optical measurements (optical expandometry) to determine the foaming behavior of polyolefin-based samples at high temperatures.

EXPERIMENTAL

Expandometry devices

Optical expandometry

An especially designed optical expandometer was initially built up in the premises of the Cellular Materials' Laboratory. The system is based on an isolating plate suspended inside a 2000 W tubular infrared heating

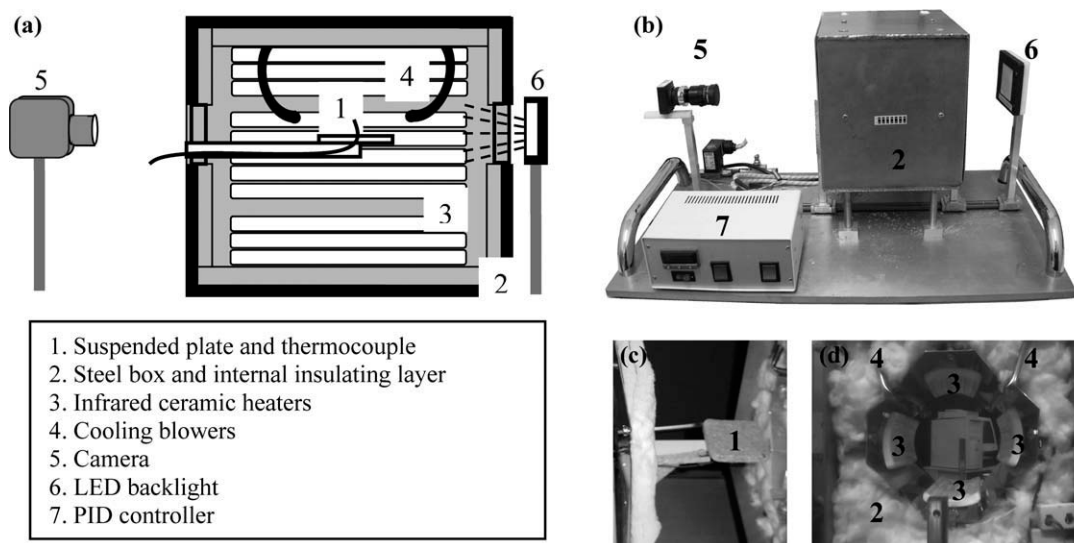


Figure 1 Schematic view of the optical expandometer.

furnace. The inner furnace consists of four symmetrically-arranged curved infrared ceramic heaters and four compressed air cooling blowers symmetrically disposed at the top part. Both heating and cooling systems are designed to provide maximum temperature uniformity. To monitor the sample's expansion, two glass windows are placed at both sides of the tubular furnace, enabling to acquire the shadow image of the free-foaming sample by setting a camera and a light source one in front of each other at opposed sides. A schematic view of the optical expandometry system, together with images depicting its external configuration and inner details of the furnace, are provided in Figure 1.

An IDS camera model UI-1485LE-C is employed, incorporating a high resolution lens (Kreuznach Xenoplan 2.8/50-0511). Although the theoretical spatial resolution according to the working distance and the field of view can be as low as 10 μm , the experimental value is closer to 20 μm . A LED backlight model INF-L-IBL-W 50/50 from Infaimon is used as light source, providing a homogenous bright back-field, facilitating the subsequent image analysis. Acquisition is conventionally carried out at 8 bits pixel depth (256 gray-level) and frame rate of 1 fps.

The temperature is controlled using a PID controller, with the input temperature being obtained from a thermocouple suspended inside the furnace. Temperature recording is synchronized with image capture. Heating ramps can be adjusted to a maximum rate of 40 K/min.

Thermal mechanical analysis

Thermo-mechanical experiments were carried out in a DMA7 from Perkin-Elmer in the TMA mode. The thickness (height) of the tested samples was measured as a

function of temperature and time using a temperature program similar to that of the optical expandometer.

The DMA7 presents four main components: a precise linear force motor, a central core rod, and measuring system assembly attached to its lower end, a high sensitivity displacement detector (LVDT) and a tubular furnace. The LVDT is the detection system of the DMA7, accurately gathering any changes in the sample's thickness. The precision of the LVDT sensor is around 2 μm . It provides high sensitivity as well as a broad dynamic range to accommodate a variety of sample sizes and geometries. The linear force motor provides precise control of all forces applied to the sample. The furnace allows the use of different temperature programs to a maximum controlled heating rate of 20 K/min. A schematic diagram of this equipment and its main components is shown in Figure 2.

Foamability tests were performed in a parallel-plate measuring configuration ($\text{Ø} = 10 \text{ mm}$). A cylindrical stainless-steel mold, opened in its upper part, was used, allowing the upper plate of the LVDT detector to be in permanent contact with the sample. The total height of the mold was of 14 mm, with an inner diameter of 11 mm and wall thickness

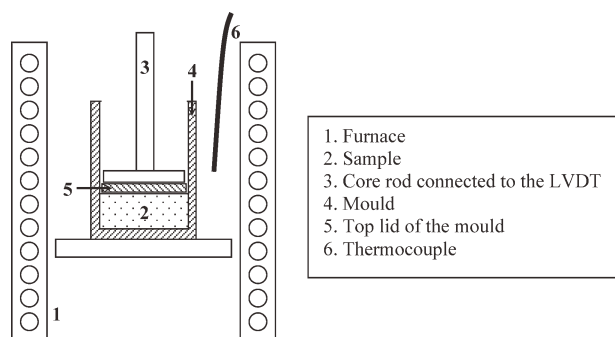


Figure 2 Schematic view of thermomechanical analyzer.

of 1 mm. The mold had a metallic 1 mm-thick lid which was placed between the sample and the top plate of the measuring system with enough fitting tolerance to prevent any sticking during expansion.

METHODOLOGY

Optical expandometry

Geometrical and experimental conditions

In contrast to foaming inside a mold, free foamed materials do not present a well defined shape, making nontrivial all volumetric expansion calculations. Two different approaches can be considered to accurately study the volumetric expansion of free-expanded materials by means of optical techniques. The first one consists in measuring the expansion in two perpendicular directions by rotating the sample or placing two cameras. A rotating-plate system has been previously applied with success to the study of the volumetric expansion.²⁰ This approach can be also carried out by independently measuring the expansion in the two directions, with the main inconvenient of requiring at least two tests for each material. The second approach is based on the use of samples with a known symmetry. For cylindrical samples and assuming uniform expansion in the radial direction, it is possible to calculate the volumetric expansion from the data obtained from only one test, as it will be explained in the subsequent section.

This second approach is the one adopted in most of the tests shown in this work, while the first one is only used for the anisotropic expansion curves (see Influence of precursor processing on the foaming uniformity subsection).

Polymer circular disks with a thickness of 3 mm were initially prepared by compression-molding in a hot-plate press IQAP-LAP PL-15. Circular preforms with a typical diameter of 11 mm were directly machined from these plates and used in the foaming experiments. In addition, circular extrusion profiles (7 mm long, 3.5 mm in diameter) were also tested.

Experiments were carried out at the maximum heating rate of the heating system to reduce the amount of collected images (1000 images are the equivalent to 5 Gb of collected data). Typical foaming tests were below 1000 s. Therefore, the temperature program used in all experiments consisted in heating, under controlled conditions, at the maximum heating rate until reaching the set-point temperature (between 190 and 215°C depending on the analyzed material) and later applying an isotherm till the foamed sample had collapsed considerably.

Image analysis

After image acquisition, an image analysis protocol based on the ImageJ software²⁶ was carried out to

extract quantitative data from the image sequence. This protocol consisted in applying to each image an edge-preserving filtering to homogenize the gray level, a subsequent binarization of the region of interest and a dimensional analysis of the growing binarized foam, all by using ImageJ conventional tools. Among all the available numerical outputs, the ones considered in this work were the projected area (number of pixels) and the minor (a) and major (b) axis of the equivalent ellipse (ellipse with the same area). The volume expansion (V) was determined using the following equation:

$$V = \frac{4}{3} \pi \cdot a \cdot b^2 \quad (1)$$

assuming uniform radial expansion.

Thermal mechanical analysis

In the case of the DMA7 system, where the sample is initially placed inside a closed cylindrical mold, data can be directly obtained without the necessity of any post-treatment, as required in optical expandometry (image analysis). In addition, the increase in height observed during foaming can be directly translated into volume expansion since growth is limited to the vertical direction. Nevertheless, as it will be shown later, this last statement is not totally accurate and a minor correction is required.

Samples used in these tests were extracted from 1 mm thick plates prepared by compression-molding in a hot-plate press. Circular preforms with a typical diameter of 11 mm were machined from these plates. A minimum of three experiments were carried out for each material.

The mold was previously coated with silicone oil to facilitate the later extraction of the foamed material. In addition, a better cap sliding was possible through silicone oil, limiting the chances of polymer sticking to the inner mold's surface.

Heating rate was selected as the maximum of the DMA7 under controlled conditions (20 K/min). After reaching the set-point temperature, it was held for the necessary time to study the foam's stabilization and collapse. The force applied during the foamability experiments was kept at zero.¹⁵

Materials and compounding

Several polyolefin-based materials specifically formulated for the foaming experiments were prepared using the following base polymers: an ethylene-propylene random copolymer, EPR (200CA10 from Inneos), and a high melt strength-based polypropylene, HMS-PP. This last one was obtained by melt-compounding using a corotating twin-screw

extruder (Collin Kneter 25 × 36D, L/D = 36) 50.0 parts per hundred (phr) of a high melt strength polypropylene (Daploy WB130HMS, manufactured by Borealis) and 50.0 phr of a linear extrusion grade-type of PP (Isplen 050 G1E, manufactured by Repsol YPF). The melt flow index (MFI) values were of 10 dg/min and 4 dg/min, both measured at 230°C and 2.16 kg, respectively, for the EPR and HMS-based formulations. Azodicarbonamide (ADC), Poro-for ADC/M-C1, supplied by Lanxess Energizing Chemistry, with a density of 1.65 g/cm³ and average particle size of 3.9 ± 0.6 μm, was used as chemical blowing agent in amounts ranging from 1.5 to 5.0 phr. Stearic acid (0.2 phr) was used as lubricant. A constant extrusion temperature profile of 165°C and a screw speed of 160 rpm were used for all the materials.

RESULTS AND DISCUSSION

Results shown in this section intend to demonstrate the validity of the optical expandometry to the study of the foamability of polymeric systems. First of all, experimental results are compared with those obtained with TMA, already used for this kind of studies in previous publications.^{15,16} After demonstrating the equivalency between both methods, different examples are displayed illustrating the usefulness of this technique to the *in situ* free foaming characterization.

Comparison between optical and mechanical techniques

Initially, one of the most important issues lies in knowing whether the optical expandometry and TMA are comparable methods and/or give equivalent results. To this end, TMA experiments were taken as reference. This task seems to be hard considering the different heating rates used in both techniques. On the other hand, the fact of having used different heating rates makes this comparison even more interesting.

Initially, if we compare the normalized volume expansion, determined by dividing the volume of the sample at a given foaming time by its initial volume, versus the foaming time, obtained with both the optical expandometer and TMA, it is possible to detect that they are significantly different [Fig. 3(a)]. Maximum expansion values and peak-times, as well as growing/collapse slopes are completely different. However, it is possible to apply a time-normalization to the curves taking the times of maximum expansion as reference [t_{ME1} and t_{ME2} shown in Fig. 3(a), respectively, for optical expandometry and TMA curves]. This normalization eliminates the heating rate differences between both experiments.

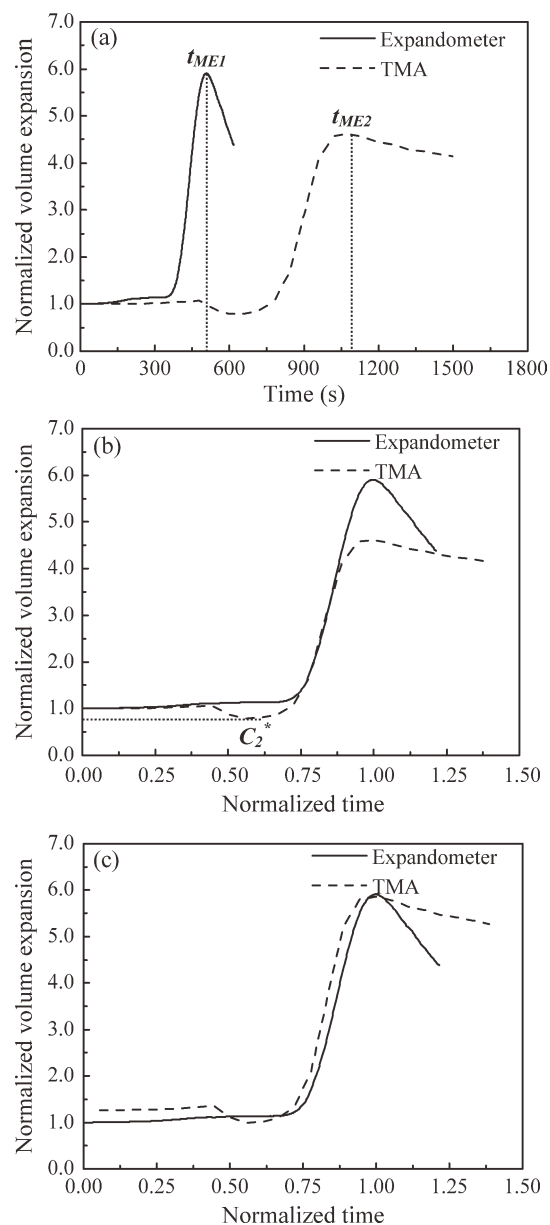


Figure 3 Curve comparison procedure using optical expandometry and TMA: (a) after volume normalization, (b) after volume and time normalizations and (c) final result after normalized volume expansion correction (PP-1.5 ADC, 205°C).

Actually, it is important to mention that the time normalization ratio (C_2/C_1) is similar to the ratio of the heating rates, that is, 2. After this normalization both curves are more similar [Fig. 3(b)], displaying parallel growing slopes. Nevertheless, there are still important differences between both curves regarding characteristics such as the maximum expansion. On the other hand, it can be observed that the TMA volume expansion curve presents a volume reduction before the foam starts to expand. This volume reduction comes from mold filling due to polymer melting, that is, due to the fact that the sample-mold fitting was not perfect, so when the precursor melts

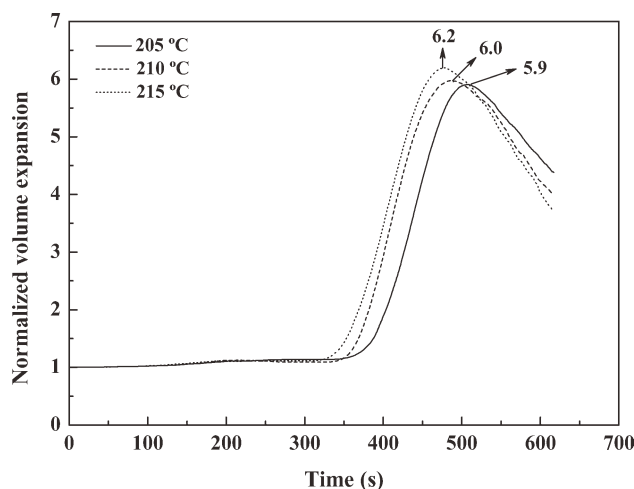


Figure 4 Expansion curves for PP-1.5 ADC at 205, 210 and 215°C.

just before ADC's decomposition it starts flowing radially, filling the whole available volume. Therefore, it was necessary to apply a volume normalization factor, C_2^* , using as reference the minimum volume registered for both curves. This procedure only alters TMA's curve. Figure 3(c) shows the final compared results after this last volume normalization. It can be observed that the maximum volume expansion is almost identical, as well as the expansion onset temperature and growing slope. Nevertheless, differences can be appreciated regarding the collapsing stage, TMA curve showing a considerably smoother decaying slope, presumably due to the friction of the material with the inner walls of the mold.

In this sense, the experimental expansion ratio determined for the HMS-based formulation was of 5.9, matching very well with the theoretical expected value based on the amount of azodicarbonamide gas yield (theoretical expansion ratio of 6).

As can be seen, the optical expandometry technique is able to characterize the foaming behavior of thermoplastic systems, with the main advantage of allowing a better measurement of the foam's decay due to the free expansion geometry, thus overcoming the problems related to sample-mold friction observed in TMA.

Influence of the foaming temperature and blowing agent content

Different foaming temperatures are expected to alter the onset of expansion, foam stabilization and final collapse. This is shown in Figure 4 by comparing the expansion behavior of an HMS-based PP formulation containing 1.5 phr of ADC (PP-1.5 ADC) at three different set-point temperatures, 205, 210, and 215°C. Being a thermally-activated process, the exothermal decomposition of the ADC is clearly acceler-

ated, even for slight temperature differences. For instance, at 215°C, the material starts growing ~ 60 s earlier than at 205°C. Maximum expansion is slightly increased with increasing the temperature. It is also important to point out that the temperature is critical for the collapsing stage. For instance, in these experiments the decaying rate is of -0.015 , -0.020 , and -0.021 NVE/s (NVE: Normalized Volume Expansion), respectively, for 205, 210, and 215°C curves, meaning that a 10°C temperature difference increases the collapsing speed up to a 40%.

Expandometry may also be used for optimizing the formulation in terms of the amount of required ADC. Comparing the foaming behaviors of two HMS-based PP formulations containing 1.5 and 3.5 phr of the same type of ADC (Fig. 5), the one with the higher concentration of ADC (PP-3.5 ADC) not only starts growing earlier (higher cell nucleation rate) but also the growing slope is steeper (0.05 and 0.12 NVE/s for 1.5 and 3.5 phr of ADC, respectively), indicating a faster cell growth rate. As expected, the maximum expansion is different for both materials: the material containing 3.5 phr of ADC expands 11 times, while the one with 1.5 phr expands 6 times.

In accordance with the expansion, the collapse of the foam with a higher amount of blowing agent also occurs faster, as deduced from the more abrupt decreasing slope after the maximum of the curve. In this particular case, the collapsing rate is approximately 3 times higher for the foam with the higher concentration of ADC.

Influence of the polymer rheology

If different formulations are compared, it is possible to see, among other effects, how the inner melt strength of the polymer affects the expansion onset.

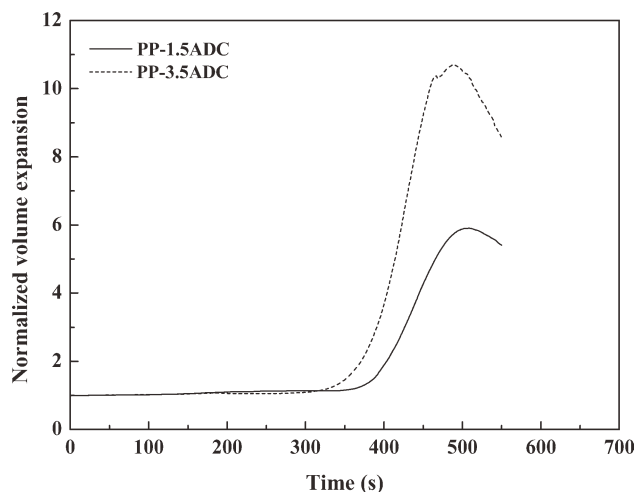


Figure 5 Optical expandometry expansion curves for the PP-1.5 ADC and PP-3.5 ADC at 205°C.

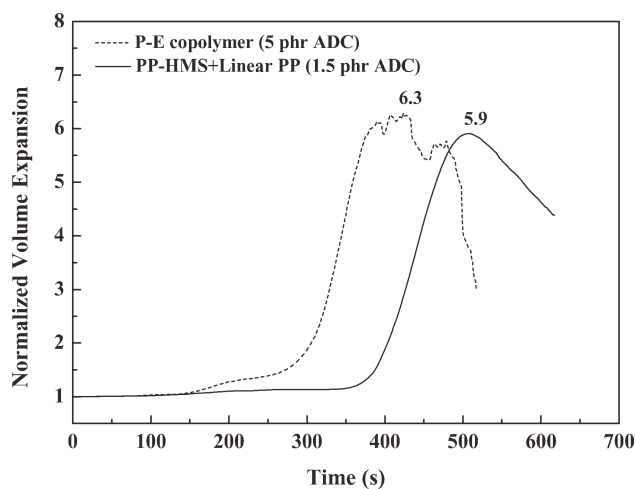


Figure 6 Compared optical expansion curves between the 5.0 phr ADC EPR copolymer and 1.5 phr ADC HMS-based formulations at a set-point temperature of 205°C.

As displayed in Figure 6, the growing stage starts considerably earlier for the EPR copolymer than for the HMS-based PP formulation, the higher melt strength and extensibility of the HMS-PP blend, alongside its considerably lower melt flow index, clearly restraining the beginning of the expansion.

Regarding the maximum expansion and expansion rate it is important to remark that although containing different concentrations of the same type of ADC (respectively, 5.0 phr for EPR and 1.5 phr for HMS-PP), both values resulted almost the same for the two materials, indicating that the rheological characteristics of both base polymers are globally

affecting their foamability. Actually, HMS-PP is a special type of PP homopolymer specifically developed for foaming applications, presenting a certain degree of long chain branching that promotes a higher melt strength and extensibility compared to more conventional linear types of polypropylenes. This is the cause why HMS-PP reaches a similar expansion than the EPR copolymer even using more than three times less blowing agent. The somewhat inefficiency of EPR as a foamable system can also be appreciated in Figure 6, exhibiting a considerably less smoother expansion than HMS-PP due to fast pore coarsening and popping. This polymeric system exhibits a considerably higher decay rate and less regular collapsing behavior. Figure 7 provides a visual observation of the progressive coarsening and collapse of the EPR system. Note that if the surface coalesced cells are thin enough, it is possible to approximately determine *in situ* their cell size.

Influence of precursor processing on the foaming uniformity

As stated previously, the optical expandometry technique allows ascertaining the expansion uniformity by examining two different directions during the expansion experiments. In the case of using circular extrusion profiles as precursors, it is possible to analyze the expansion in the two main directions, radial and axial, of the circular extrusion profile. Figure 8(a) shows the normalized expansion (NE) versus time for the two mentioned directions.

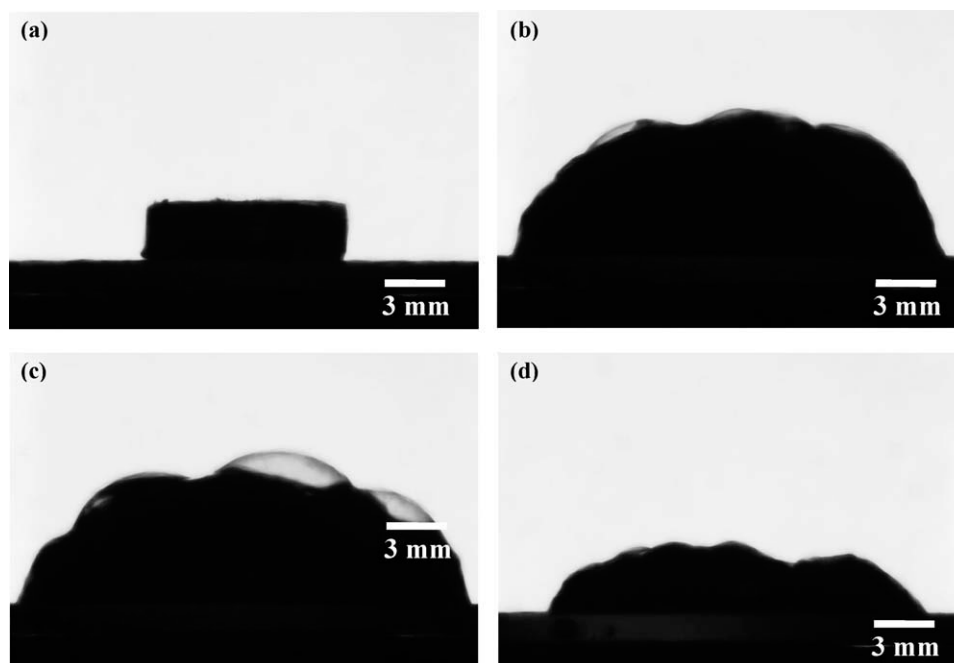


Figure 7 Optical expandometry photos taken at different times for the EPR copolymer: (a) at the beginning; (b,c) showing increasingly higher bubble coalescence; (d) after complete collapse.

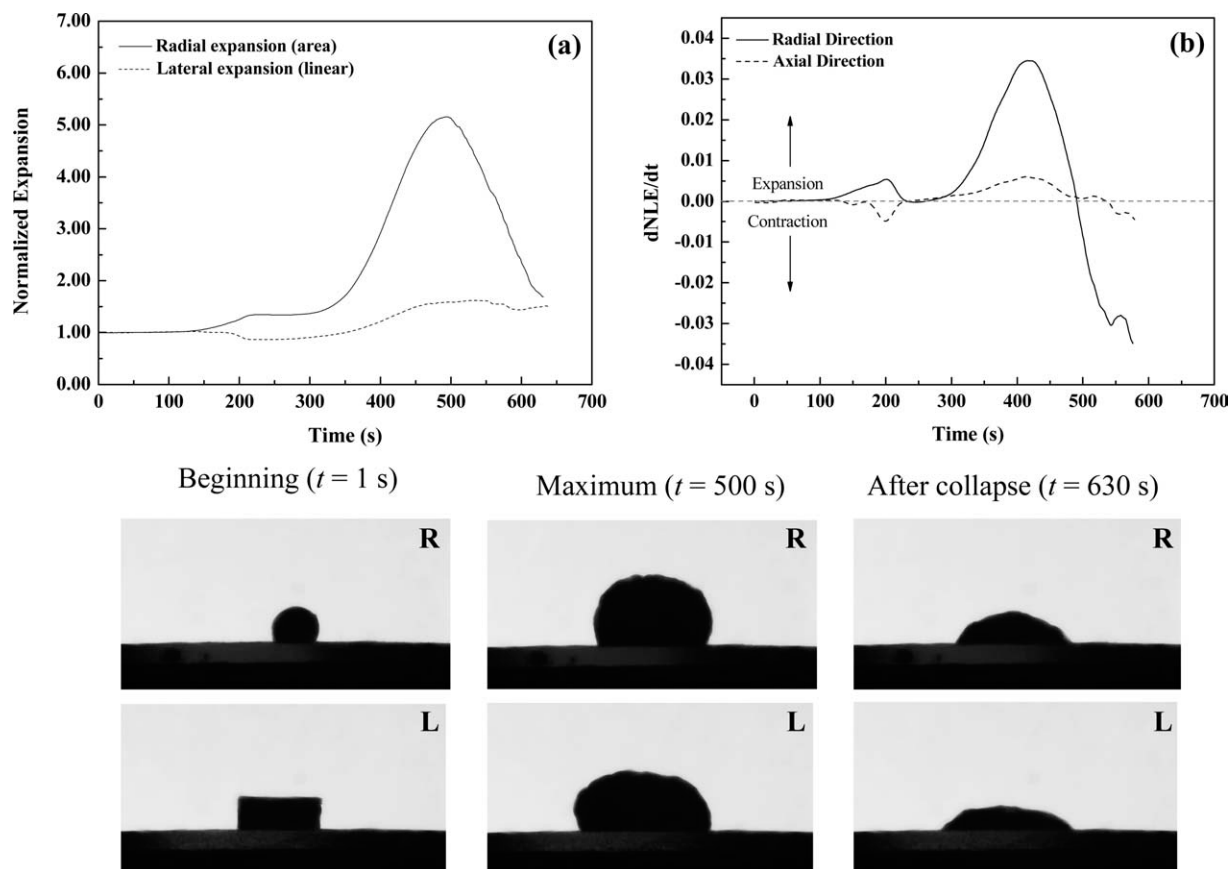


Figure 8 Radial (R) and lateral (L) optical expandometry: (a) expansion curves and (b) respective derivatives for the circular extrusion profile and photos taken at the beginning ($t = 1$ s), maximum ($t = 500$ s) and after foam collapse ($t = 630$ s).

Alongside the important differences that can be registered between both expansions and the visual information that can be gathered, it is possible to calculate the time derivative of the NE in the radial and axial directions, as depicted in Figure 8(b). As it is clearly observed, the material shrinks in the axial direction and expands in the radial one during melting, related to the anisotropic crystalline orientation of the solid precursor material. The later lower expansion in both radial and axial directions is not only a consequence of the material's anisotropy but also the result of a shape factor effect.

CONCLUSION

The novel optical method and image analysis methodology to determine foam expansion presented in this work has been demonstrated to give precise reproducible volumetric expansion measurements of chemically foamed thermoplastic polymeric systems.

This technique has several advantages over conventional thermomechanical techniques, such as:

Possibility of measuring an accurate volumetric expansion without the need of a mold (free expansion), eliminating contact problems that may affect the measurements.

Since it is a noncontact method, it is possible to measure the foam evolution without affecting the material's expansion and collapse. The thermal inertia of the mold is thereby eliminated.

Compared to foaming inside a mold, there is no preferential unidirectional expansion. Therefore, it is possible to analyze multidirectional and eventually anisotropic foam expansions in a single experiment.

It enables the *in situ* observation of the stability and cell coalescence/coarsening of the foams, that is, apart from the numerical results, some visual information can be gathered.

Measurements are faster than with TMA, and although the output is not numerical, the image analysis methodology applied later on can be automatically performed.

In conclusion, a novel optical expandometry technique has been demonstrated to be a very helpful tool for the analysis of the foaming mechanisms of thermoplastic-based materials, enabling the study of tailor-made foaming formulations for the most varied applications.

References

1. Gibson, L. J.; Ahsby, M. F. *Cellular Solids: Structure and Properties*, 2nd ed.; Pergamon Press: Oxford, 1998.
2. Eaves, D. *Handbook of Polymeric Foams*; Rapra Technology Limited: Shawbury, 2004.
3. Lee, S. T. In *Polymeric Foams: Mechanism and Materials*, 1st ed.; Lee, S. T., Ramesh, N. S., Eds.; CRC Press: Florida, 2004, Chapter 1.
4. Rodríguez-Pérez, M. A.; de Saja, J. A. *Cell Polym* 1999, 18, 1.
5. Park, C. P. In *Polymeric Foams and Foam Technology*, 2nd ed.; Klempner, D., Sendjarevic, V., Eds.; Hanser: Munich, 2004, Chapter 8.
6. Martínez-Díez, J. A.; Rodríguez-Pérez, M. A.; de Saja, J. A.; Arcos y Rábago, L. O.; Almanza, O. A. *J Cell Plast* 2001, 37, 21.
7. Rodríguez-Pérez, M. A. *Adv Polym Sci* 2005, 184, 87.
8. Jennings, R. *J Cell Plast* 1969, 5, 159.
9. Rowton, R. L. *J Cell Plast* 1980, 16, 287.
10. Van Thuyne, A.; Zeegers, B. J. *J Cell Plast* 1978, 14, 150.
11. Jianqiu, Y.; Jianyaun, Z.; Dening, W.; Chumpu, H.; Shengkang, Y.; Yiou, C.; Yufu, C.; Ziquian, X.; Jin, S.; Yin, W. *J Cell Plast* 1990, 26, 39.
12. Baser, S. A.; Khakhar, D. V. *J Cell Plast* 1993, 29, 280.
13. Taki, K.; Yanagimoto, T.; Funami, E.; Okamoto, M.; Ohshima, M. *Polym Eng Sci* 2004, 44, 1004.
14. Tsivintzelis, I.; Angelopolou, A. G.; Panaviotou, C. *Polymer* 2007, 48, 5928.
15. Velasco, J. I.; Antunes, M.; Ayyad, O.; Saiz-Arroyo, C.; Rodríguez-Pérez, M. A.; Hidalgo, F.; de Saja, J. A. *J Appl Polym Sci* 2007, 105, 1658.
16. Velasco, J. I.; Antunes, M.; Ayyad, O.; López-Cuesta, J. M.; Gaudon, P.; Saiz-Arroyo, C.; Rodríguez-Pérez, M. A.; de Saja, J. A. *Polymer* 2007, 48, 2098.
17. Banhart, J. *Prog Mater Sci* 2001, 46, 559.
18. Banhart, J.; Weigand, P. In *Metal Foams*; Banhart, J., Eifert, H., Eds.; Verlag MIT: Bremen, 1998, p 13.
19. Duarte, I.; Banhart, J. *Acta Mater* 2000, 48, 2349.
20. Rodríguez-Pérez, M. A.; Solórzano, E.; García-Moreno, F.; de Saja, J. A. In *Porous Metals and Metallic Foams*; Lefebvre, L. P., Banhart, J., Dunand, D., Eds.; DEStech Publishers: Pennsylvania, 2008, p 75.
21. Banhart, J.; Stanzick, H.; Helfen, L.; Baumbach, T. *Appl Phys Lett* 2001, 78, 1152.
22. Rack, A.; Garcia-Moreno, F.; Baumbach, T.; Banhart, J. *J Synch Rad* 2009, 16, 432.
24. García-Moreno, F.; Fromme, M.; Banhart, J. *Adv Eng Mater* 2004, 6, 416.
25. Hurnik, H. In *Plastics Additives Handbook*, 5th ed.; Zweifel, H., Ed.; Hanser: Munich, 2001, Chapter 13.
26. Naguib, H. E.; Park, C. B.; Reichelt, N. *J Appl Polym Sci* 2003, 91, 2661.