Anomalous Thickness Increase in Crosslinked Closed Cell Polyolefin Foams During Heat Treatments

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ABSTRACT: When crosslinked closed cell polyolefin foams are under a temperature above the melting point of the base polymer, a reduction of their size is expected due to the gas diffusion out of the foam. However, some kinds of crosslinked closed cell polyolefin foams present one direction (thickness direction) in which the foam size increases during the first minutes of the thermal treatment. The thickness of the foams after the thermal treatment can be higher than the thickness of the original foams. An experimental study is presented on the thickness increase, as well as on the changes in the dimensions and the properties of foams with different densities, which were obtained from different foaming processes and made of different base polymers, as a function of the treatment temperature and the treatment time. This investigation sought to discover the physics mechanisms that control the anomalous thickness increase. The experimental results show that the thickness increase of these materials is related to the anisotropic cellular structure of the original foams. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2825–2835, 1999

Key words: polyolefin foams; thermal treatments; thermal expansion; foams with anisotropic properties; thermoforming

INTRODUCTION

In recent years, foamed polyolefins have been able to steadily increase their market share by entering new applications segments. These materials show a variety of advantageous properties, such as their thermoplastic character, which allow their application in a wide range of postfabrication techniques, and their closed cell structure that leads to a low level of water absorption, low water transmission, no dust absorption, good aging, good impact insulation, and so forth. When structured as crosslinked foams, these materials have an extended working temperature range, present a high resistance to chemicals, and have good stability against weathering and ultraviolet radiation. Furthermore, the polyolefinic composition plays an important role in modern industry for the development of applications when the use of a uniform polymer is necessary. This aspect is also particularly useful for practical recycling procedures.

Some postfabrication techniques (vacuum forming, press molding, lamination, etc.) are used in the manufacture of products (objects) made of crosslinked closed cell polyolefin foams.[1] In these postfabrication techniques, heat is applied to the foam. Usually, the temperature is above the melting temperature of the polymer that comprises the cell walls of the foam. Under these conditions

Table I Chemical Composition and Density of Materials Under Study

Kind of Foam	Material	Chemical Composition	Density (kg/m^3)
Alveolen	NT0405	60% LDPE, 40% HDPE	289.2
	NT0805	60% LDPE, 40% HDPE	115.1
	NT2008	60% LDPE, 40% HDPE	54.2
	NT2510	60% LDPE, 40% HDPE	41.3
	NA2012	100% LDPE	51.6
	NA3308	100% LDPE	31.2
Alveolux	XA0805	100% LDPE	104.7

a reduction of the size of these materials is expected due to the gas diffusion out of the foam. However, if the heating above the melting temperature of the base polymer is studied for some kinds of crosslinked closed cell polyolefin foams, it is possible to observe that there is one direction (thickness direction) in which the foam size increases during the first minutes of the heating process. The thickness of the foams after a thermal treatment can be higher than the thickness of the original foams.

Although from an applied point of view it could be difficult to control and optimize the properties of the foam after the thermoforming process, the published literature contains very little information about the effect of thermal treatments on the structure and properties of foams. The size and the consequent density, cellular structure, and macroscopic properties of the foams change during the treatments. Because of these reasons it is very important to study these changes: first, to discover the physics mechanisms that control the behavior and, second, to control and optimize the different thermoforming processes.

In this work, an experimental study is presented on the thickness increase, change in dimensions, and change in properties of a collection of crosslinked closed cell polyolefin foams with different densities, which were obtained from different foaming processes and made of different base polymers, as a function of the treatment temperature and treatment time.

EXPERIMENTAL

Materials

The acronyms, density, and chemical composition of the materials under study are summarized in Table I. These foamed samples are made of crosslinked polyolefins and were kindly provided

by Sekisui Alveo BV (Roermond, The Netherlands). Two kinds of foams can be distinguished: Alveolen (N) and Alvelolux (X).

Alveolen Foams (N Foams)

Continuous roll foams are produced by sheet extrusion of a polyolefin compound containing a foaming agent. The solid sheet is crosslinked by a high-energy electron bean before the foaming agent in the sheet is heat activated. The foaming process is carried out in a horizontal plane. This means that the foamable sheet passes horizontally through a hot air heated foaming oven. The expanding sheet is carried out on a belt and sup-

Figure 1 (a) Nomenclature used to characterize the sheet directions in the Alveolen foams. (b) Nomenclature used to characterize the sheet directions in the Alveolux foams.

ported by an air layer. After expansion the foams are passed through cooling rolls and are wound up.

The nomenclature used to characterize the sheet directions, machine direction (MD), transverse direction (TD), and thickness direction (ED) is shown in Figure 1(a).

Foams of two different chemical compositions were studied. NT foams were made of blends with a 60% low-density polyethylene (LDPE) content and a 40% high-density polyethylene (HDPE) content. NA foams were made from 100% LDPE sheets.

Alvelolux Foams (X Foams)

In this process the polyolefin is compounded with the foaming agent and a peroxide crosslinking agent. The compound is placed in a mold and heated in a heavy-duty press to enable crosslinking and to decompose the foaming agent to release the gas for expansion. The material may be removed hot from the press to produce the foam directly (in a density range above 70 kg/m^3) or it may be cooled and expanded separately in a second mold. The two-stage process is normally used for densities below 70 kg/m^3.

These materials are not made in a continuous process; therefore, they have two equivalent directions (D1 and D2) and the thickness direction. The nomenclature used to characterize the Alveolux foams is shown in Figure 1(b).

One Alveolux foam (XA0805) was studied. LDPE was used as the matrix polymer for this material (Table I).

Thermal Treatments

Two kinds of thermal treatments were carried out.

In the first foam sheets, as received from the company, were cut in square samples (3-cm sides) and introduced in an oven at a temperature T_t (treatment temperature) and for a time t_t (treatment time). The foam samples were hung from the ceiling of the oven by a thin copper thread that went through the material. The materials were only in contact with the hot air and the thin copper thread. The effect of the thread was insignificant and due to this reason it can be said that the heating of the materials was isotropic, which implies there were not privileged directions. The experimental results were related to the anisotropic cellular structure of the foams and, to avoid

problems with the explanations of the results, it was convenient to choose a kind of thermal treatment with an isotropic heating.

Some preliminary experiments were carried out with the samples between two hot plates. The qualitative behavior of each foam was the same as in the experiments previously explained. Therefore, the experimental trends of the results presented in this work do not depend on the geometric arrangement of the samples in the oven.

The treatment temperatures and times were chosen taking into account the usual temperatures and times used for the thermoforming of these materials: between 120 and 160°C for the temperature and between 1 and 10 min for the time. Experiments with a time of 30 min were also made.

In the second treatment the thickness of the materials was directly measured as a function of the treatment time by using a thermomechanical analyzer, which measures the change in length of a material as a function of the temperature or as a function of the time.

The thermomechanical analysis (TMA) was conducted on Perkin–Elmer DMA7 test equipment. The applied stress was 130 Pa, which is sufficient to ensure that the probe remains in contact with the sample and small enough to allow the compression strain to be neglected. These tests were performed with a parallel plate measurement system. The plate diameter was 10 mm and the test specimens were prepared in a cylindrical shape with the same diameter.

After each thermal treatment (first or second) the samples were taken out of the oven and before their physical characterization were stored at room temperature for 1 month. Although the size of the foams did not change during the storage period, the sample weight increased because of the absorption of water vapor by the foam. After 1 month the weight of all the foams reached a constant maximum value.

Both thermal treatments present a problem related to the stabilization of the treatment temperature in the first seconds of the experiments. The oven is opened to introduce the samples and this decreases the treatment temperature. In order to avoid problems in the comparison of the foam behavior, the time used to introduce the foams in the oven was kept constant for all the materials. Consequently, each foam material was tested under the same experimental conditions.

In order to obtain an average response, the two kinds of thermal treatments were repeated 3

times for each foam and for each thermal treatment.

Foam Characterization

Before each thermal treatment and after the thermal treatments and the storage period, the samples were characterized using the following experimental methods.

Size and Weight Determination

The foam sizes in the MD and TD were measured using a gauge; the thickness of each foam was obtained using the thermomechanical analyzer DMA7, and the foams were weighed using a Mettler AT261 balance.

Density Measurements

Density measurements were performed by Archimedes' principle using the density determination kit for the AT261 Mettler balance.

Differential Scanning Calorimetry (DSC)

Thermal properties were studied by means of a Mettler DSC30 differential scanning calorimeter, which was previously calibrated with indium. The weights of the samples were approximately 3.5 mg. The experiments were performed between −40 and 200°C at 10°C/min.

Scanning Electron Microscopy (SEM)

Quantitative image analysis was used to assess the type of cellular structure, the mean cell size, and the anisotropy ratio. For this purpose, cross sections of extrudate were microtomed at low temperature to provide a smooth surface that was vacuum coated with gold and examined by SEM using a JEOL JSM 820. Each micrograph was analyzed by obtaining data from 10 reference lines. The apparent mean cell size was estimated by calculating the number of cells that intersected each reference line and dividing the appropriate reference length by the number of cells.[2]

Foams usually present anisotropic properties due to their cell shape. In general, the cells have a higher size in the parallel direction to the foaming direction[3] (cells are elongated in the foaming direction). For the Alveolen foams, the cell size is different for each one of the three principal directions: the MD, TD, and ED.[4] The degree of anisotropy can be characterized by means of the ratio between the larger and the smaller cell size.[5]

Wide-Angle X-ray Diffraction (WAXD)

WAXD experiments were performed using a Philips powder 1050/71 diffractomer (CuK$_\alpha$, nickel filtered radiation). Radial scans of intensity (I) versus scattering angle (2θ) were recorded in the reflection scanning mode (range 5–40°).

The scans were taken from the three perpendicular principal directions. These experiments were used to study the orientation of the crystalline phase of the matrix polymer of each foam.[6–8]

Thermal Expansion Experiments

The linear thermal expansion coefficient can be determined from

$$\alpha = \frac{1}{l_0} \frac{dL}{dT} \tag{1}$$

where l_0 is the original length at a reference temperature (25°C in this work) and L is the length of the sample at a temperature T.

The measurements were conducted on Perkin–Elmer DMA7 test equipment with the same geometric arrangement as in the second kind of thermal treatments previously explained. Test specimens were prepared in a cubic shape.

To obtain the thermal expansion coefficient out of the range where thermal transitions were present,[4] experiments were performed between 5 and 25°C at a heating rate of 1°C/min maintaining the test sample at 5 and 25°C during 15 min. Each type of material was scanned 3 times. The linear thermal expansion coefficient was measured in the three principal directions of each foam sample.

Functions Used to Characterize Effect of Thermal Treatments

To characterize the change in the properties of its foam during the thermal treatments, relative functions were used for each physical property. For example, the relative change in thickness was calculated by means of

$$\Delta t(t) = \frac{t(t) - t_0}{t_0} 100 \tag{2}$$

where $t(t)$ is the thickness of the foam as a function of the treatment time and t_0 is the original foam thickness (before the treatment).

Figure 2 Thermal behavior of the NT0805 original foam and thermal behavior of this material after thermal treatments at 160°C for 1, 2.5, 5, 10, and 30 min.

Similar functions were used to characterize the relative change in MD, TD, weight, and density.

RESULTS

Microscopic Characterization

DSC

The thermal behavior of the NT0805 original foam and the thermal behavior of this material after the treatments at 160°C for 1, 2.5, 5, 10, and 30 min can be observed in Figure 2. No significant differences between the thermograms were observed (except for the foam treated for 1 min); therefore, the morphology of the crystalline phase of the matrix polymer does not change as a consequence of the heat treatment and the storage period. This result was found for all the foams under study.

The LDPE melting peak is slightly different for the NT0805 foam treated for 1 min. One possible explanation for this behavior could be that, because of the low thermal mass of the foams,[3] the temperature of the foam in the oven during the 1-min treatment did not reach a value higher than the melting temperature of the LDPE phase (110°C). Therefore, the LDPE crystals were not completely melted during the treatment, which could result in a slightly different morphology of the LDPE crystalline phase of this foam.

WAXD

The WAXD patterns for the NA3308 original foam, taken from two of the three perpendicular directions, are presented in Figure 3(a). In order to evaluate the degree of the orientation of the crystalline phase, the ratio of the intensity between the (110) to that of the (200) reflection can be calculated.[6] It is clear that this intensity ratio $I(110)/I(200)$ was different for each direction. This implies that the crystalline phase of the original foams is oriented. This result was also found for the other original Alveo foams.

When the same intensity ratio is analyzed for the NA3308 treated foam [treated for 20 min at 160°C; Figure 3(b)], it can be concluded that this material also has an oriented crystalline phase; therefore, the crystalline structure of the matrix polymer of the treated materials is very similar to that of the original foams.

SEM

A typical image of the cellular structure of the original Alveolen foams is shown in Figure 4(a) (NT0805 foam). In this micrograph, the section on one foam cut parallel to the machine direction can be observed. This foam presents anisotropic cells and a larger cell size in the direction parallel to the foaming direction.

The materials have anisotropic cells due to the foaming process. In this foaming method the sheet is passing horizontally through a hot air heated foaming oven; consequently, the sheet is stretched during the expansion, which results in elongated cells in the machine direction.[9]

The cellular structure of an Alveolux foam can be observed in Figure 4(b). This material was not stretched during its expansion; consequently, its cells were almost spherical. Thus, this foam was almost isotropic.

A typical example (NT0805) of the cellular structure after a treatment at 160°C for 1, 2.5, 5, 10, and 30 min can be observed in Figure 5. The cellular structure after a treatment of 1 min is very similar to that of the original foam. However after the 2.5, 5, 10, and 30 min treatment, the cells of the material were found to be almost spherical. While the cell size in the thickness direction increased, the cell size in the other two directions decreased during the treatment. Therefore, the anisotropy ratio decreased as well.

Macroscopic Behavior

Effect of Treatment Temperature

It was observed that the dimensions of the foams remained unchanged when the temperature of

Figure 3   (a) X-ray diffraction pattern of the NA3308 original foam taken from two of the three principal directions. (b) X-ray diffraction pattern of the NA3308 foam treated for 20 min at 160°C taken from two of the three principal directions.

(a)

(b)

Figure 4 (a) Micrograph of the NT0805 foam in the direction parallel to the foaming direction. (b) Micrograph of the XA0805 foam.

the thermal treatment was under the melting temperature of the matrix polymer. Therefore, the change in the dimensions of the foams are caused by the thermal treatments above the melting temperature of the base polymer.

Effect of Treatment Time

Figure 6 refers to the relative change in thickness $\Delta t(t)$ measured with the thermomechanical analyzer for a treatment temperature of 160°C in some of the foams under study. It can be seen that the Alveolen foams have a quick thickness increase at low treatment times. After some minutes the thickness begins to decrease, and after a critical time the foam thickness is the same as that of the original foam ($\Delta t(t) = 0$). The Alveolux foam does not present the thickness increase

at low treatment times (Fig. 6). For this foam the thickness decreases when the treatment time increases.

The relative change in the size of the MD and TD are shown in Figure 7 for some of the foams. The two quantities are negative for both Alveolen and Alveolux foams; therefore, the foam sizes in these two directions decrease when the treatment time increases. It is significant to take into account that while this decreasing is higher in the MD than in the TD for the Alveolen foams, the decreasing is almost equal in the D1 direction and in the D2 direction for the isotropic Alveolux foam.

The relative change in thickness for a treatment time of 10 min, $\Delta t(t = 10$ min), as a function of the anisotropy ratio of the original NT foams is shown in Figure 8. It can be observed that the thickness increase is higher for the more anisotropic foams.

Weight and Density as Function of Treatment Time

The relative change in weight and density for a treatment at 160°C and for different treatment times can be observed in Table II.

The sample weights decrease when the treatment time increases. To explain this result two different contributions must be taken into account: the water vapor present in the original foams evaporates at 160°C, and at this high temperature part of the gas present in the samples diffuses out of the foam.

In order to separate these two contributions, the samples were stored at room temperature for 1 month. The foams absorb water vapor and after 1 month the foam weight had reached its maximum value (measured with an accuracy of 10^{-2} mg). Consequently, the difference between the original weight and the weight after the thermal treatment and a period of storage of 1 month was approximately the weight of the diffused gas from the foam.

For the Alveolen foams the density slightly decreases in the first minutes of the treatment process; later, this density begins to increase. After some time (this time depends on the material) the density becomes higher than that of the original foam. For the Alveolux foam the weight, the thickness, and the sizes in the D1 and D2 directions decrease; therefore, the density increases as a function of the treatment time.

Figure 5   Micrographs of the NT0805 foam treated at 160°C for different treatment times: (a) 1 min at 160°C, anisotropy ratio ≈ 1.35; (b) 2.5 min at 160°C, anisotropy ratio ≈ 1.18; (c) 5 min at 160°C, anisotropy ratio ≈ 1.06; (d) 10 min at 160°C, anisotropy ratio ≈ 1.04; and (e) 30 min at 160°C, anisotropy ratio ≈ 1.04.

Figure 6 Relative change in thickness as a function of the treatment time for a thermal treatment at 160°C.

Figure 8 Relative change in thickness for the NT foams for a thermal treatment at 160°C for 10 min as a function of the anisotropy ratio of the original foams.

TMA

From the previous results it can be concluded that the cellular structure of the foams change after the treatments. The cells in the original foams were elongated in the parallel direction to the foaming direction and present an almost spherical shape in the 30-min treated foams. The density of the foams also changes.

In order to verify this microscopic observation, the thermal expansion in the three principal directions of the foams was measured.

Some changes in the macroscopic properties could be expected. One example (NT0805 foam) of the thermal expansion of the foams under study can be seen in Figure 9. It is clear that for the three principal directions the linear thermal ex-

pansion coefficient of the treated foam (at 160°C for 30 min) is different than that of the original sample.

The linear thermal expansion in the thickness direction increases because of the higher cell size of the treated foam in this direction. The thermal expansion in the other two directions (MD and TD) decreases due to the lower cell size of the foams in these directions.

DISCUSSION

It is worthy to discuss two important experimental results:

1. For the Alveolen foams there is an anomalous thickness increase during the first minutes of the thermal treatments.
2. The reduction of the size of the foams after the first minutes of the thermal treatment.

These two experimental results can be rationalized taking into account the two main factors that control the behavior: the anisotropic cellular structure of the original foams and the gas diffusion from the foams.

The anomalous thickness increase seems to be related to the anisotropic cellular structure of the original foams. Three experimental results support this hypothesis.

The matrix polymer morphology does not change significantly after the thermal treat-

Figure 7 Relative change in the machine and transverse directions as a function of the treatment time for a thermal treatment at 160°C.

Table II Weight and Density for Foams Treated at 160°C for Different Times

	Δ Weight (%) ($t_t = 1$ min)	Δ Density (%) ($t_t = 1$ min)	Δ Weight (%) ($t_t = 10$ min)	Δ Density (%) ($t_t = 10$ min)	Δ Weight (%) ($t_t = 30$ min)	Δ Density (%) ($t_t = 30$ min)
NT0405	−0.01	−1.74	−0.07	4.85	−0.08	17.68
NT0805	−0.01	−0.05	−0.07	1.78	−0.14	13.42
NT2008	−0.05	−10.07	−0.27	−4.91	−0.45	0.81
NT2510	−0.01	−11.18	−0.32	−5.61	−0.57	−0.29
NA2012	−0.04	−11.72	−0.56	−10.38	−0.85	−5.29
NA3308	−0.13	−9.46	−0.78	−6.75	−0.95	−3.2
XA0805	−0.13	7.47	−0.30	63.05	−0.35	254.5

ments. Therefore, the matrix polymer could not be mainly responsible for the thickness increase.

The isotropic Alveolux foam does not present this phenomenon.

After a thermal treatment the cellular structure of the foams changes and becomes more isotropic. Moreover, the thickness increase is higher for the more anisotropic foams.

Another important factor that could account for the thickness increase is a possible reexpansion of the foam due to rests of the foaming agent present in the original foams. However, the experimental results show that this is not the reason for the thickness increase, because this phenomenon appears at temperatures (approximately 115°C for the NA foams) below the temperature of activation of the foaming agent (approximately 160°C).

The release of the matrix polymer orientation could also be responsible for the change in the dimensions of the foams, but from the WAXD experiments it can be observed that this release of orientation is not significant for these materials in the range of time and temperature treatments where the thickness increase occurs.

The foam behavior as a function of the treatment time could be explained as follows. The two main factors that control the behavior have a different dependence on time: while the foam anisotropy is more important during the first minutes of the heating process, the gas diffusion is more important after the first minutes of the treatments.

In the first minutes of the treatment and at higher temperatures than the melting temperature of the matrix polymer, the gas pressure in the foams increases and the matrix polymer becomes softer. The gas pressure tries to deform each cell. If the cell is anisotropic, it is easier to deform the cell in the direction of lower size (thickness direction); consequently, it is possible to reach an increase in the cell size in this direction, which would explain the thickness increase. The cell size should decrease in the other directions (MD and TD). The cell size is higher in the MD than in the TD for the original foams[4]; therefore, the change in the cell size in the MD should be higher for the Alveolen foams. These changes in cell size result in a change in the dimensions of the foams.

When the treatment time increases the foam becomes more isotropic, then under these conditions it is more difficult for the gas pressure to deform each cell. Moreover, when the cell walls become softer, it is easier for the gas to diffuse out of the foam. The gas diffusion is proved by the weight reduction of the foams. Hence, the thickness of the foam and the size in the MD and TD decreases and it begins to increase the density.

Figure 9 Thermal expansion coefficient in the three principal directions for the NT0805 original foam and for the NT0805 foam after a treatment at 160°C for 30 min.

The Alveolux foam is an isotropic material; therefore, the thickness increase does not occur for this foam for which the gas diffusion controls the foam behavior.

Other experimental results can be rationalized, taking into account the previous explanations.

The density of each Alveolen material decreases in the first minutes of the treatments due to the thickness increase; later the density increases due to the size reduction and to the gas diffusion out of the cells. For the Alveolux foam the thickness increase does not occur; therefore, the density decreases when the treatment time increases.

The different behaviors of the two kinds of foams is the explanation for the very different values of the density increase after the same treatment (Table II).

Finally, the thermal expansion coefficient depends on the cellular structure of the foams. Because of this reason, this physical property is sensitive to the changes in the cellular structure that take place during the thermal treatments.

CONCLUSIONS

The anomalous thickness increase, as well as the change in the dimensions and in the properties, of some crosslinked closed cell polyolefin foams were studied as a function of the temperature and time treatments.

It was shown that the change in the dimensions appears at treatment temperatures higher than the melting temperature of the base polymer.

Anisotropic foams present an initial thickness increase and after some minutes the thickness begins to decrease. The size in the MD and TD decrease as a function of the time. The density of the Alveolen foams first decreases and later increases as a function of the treatment time.

Isotropic foams do not present the thickness increase. The weight and size of the foam decreases as a function of the treatment time; consequently, the density increases.

The physics mechanisms that control the previous behavior are related to the anisotropic cellular structure of the original foams, which causes the initial thickness increase, and to the diffusion of the gas from the foams, which causes the size reduction.

Furthermore secondary results were found in this investigation. The crystalline phase of the foams is oriented, the treatment does not change the morphology of the crystalline phase of the matrix polymer in the foam, and the linear thermal expansion of the treated foams depends on the cellular structure.

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