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(71) Applicant *(for all designated States except US)*: **DOW GLOBAL TECHNOLOGIES INC.** [US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **SUBRAMONIAN, Suresh** [US/US]; 410 Belrose Drive, Cary, NC 27513 (US). **FILICCIA, Phillip** [US/US]; 6036 Quartz Lane, Grand Blanc, MI 48439 (US).

(74) Agent: **TREANGEN, John, B.**; The Down Chemical Company, Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

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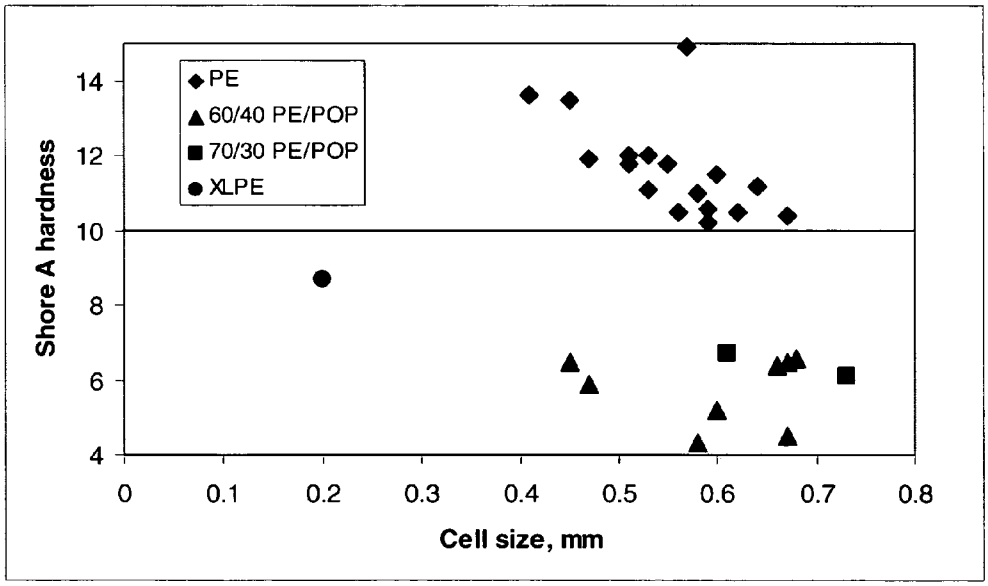

Figure 4: Shore A Hardness of PE/POP, PE & XLPE Foams

(57) **Abstract:** A continuously extruded non-crosslinked polyolefin foam comprising a) a blend of a base resin such as low density polyethylene (LDPE) and a modifier resin b) a permeability modifier and c) a nucleator, and a process of manufacturing the foam.

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SOFT TOUCH POLYOLEFIN FOAM

BACKGROUND AND SUMMARY OF THE INVENTION

The present invention relates to a polyolefin foam, preferably a continuously extruded, non-crosslinked, fine cell, soft touch polyolefin foam, a process of manufacturing the foam product, and an article comprising the foam product. The foam of the present invention comprises a) a blend of a base resin such as low density polyethylene (LDPE) and a modifier resin b) a permeability modifier and c) a nucleator.

Microcellular crosslinked polyolefin foam has been the material of choice for automotive materials handling applications. However, such foams are generally not recyclable. Therefore, environmental pressures have created an unmet market need for a 100% recyclable replacement product.

Vinyl and nitrile rubber foams have been the materials of choice for athletic sports gear (e.g. hunting jackets, athletic pads and gym mats) and buoyancy equipment (e.g. life vests, personal flotation devices). However, these materials are not recyclable and the cost of making the products by these materials is high. Therefore, market pressures have created an unmet need for a low cost replacement product.

Accordingly, there is a need to develop a recyclable dimensionally stable foam to meet the performance requirements for various foam applications at low cost. Preferably, such foam is a non-crosslinked, fine cell, soft touch foam made of thermoplastic polyolefin materials. Therefore, it is an object of the present invention to provide such a foam and a process for manufacture thereof.

An accumulating extrusion process has been used in the past to make polyolefin foam having fine-celled structure. However, the accumulating extrusion process is discontinuous. In such a process, the polymer melt is extruded in a holding zone (accumulator) and periodically ejected by a movable ram out into ambient conditions where unrestrained foam expansion occurs. In contrast, a continuous extrusion process is employed in the present invention. A continuous extrusion process is advantaged over a discontinuous process in terms of more consistent product quality (e.g. uniform fine cell foam having a flat profile) and lower processing cost.

By properly formulating the composition (resin, blowing agent, and additives) and setting the correct process conditions, the present invention has shown that a dimensionally stable and fine cell foam can be produced over a broad density range on a continuous extrusion line without folding or warping problems.

More specifically, the present invention provides a polyolefin foam, preferably a non-crosslinked and soft touch foam, comprising:

a) a resin blend of a base resin and a modifier resin,

b) a permeability modifier, and

c) a nucleator.

The base resin comprises a low density polyethylene (LDPE) and the modifier resin comprises a substantially linear polymer of α-olefin.

Preferably, the foam is a continuously extruded polyolefin foam that is substantially free of corrugation.

In one preferred embodiment, the substantially linear polymer of α-olefin comprises a homopolymer of a C2-C20 α-olefin or an interpolymer with at least one C3-C20 α-olefin and/or a C4-C18 diolefin; more preferably, the substantially linear polymer of α-olefin is a low modulus polyolefin plastomer (POP).

In another preferred embodiment, the soft touch foam comprises fine cells in a substantially closed cell structure.

According to one aspect, the present invention provides an article comprising a polyolefin foam. Preferably, the foam is a non-crosslinked and soft touch polyolefin foam. The foam comprises:

a) a resin blend of a base resin and a modifier resin,

b) a permeability modifier, and

c) a nucleator,

The base resin comprises a low density polyethylene (LDPE) and the modifier resin comprises a substantially linear polymer of α-olefin. Preferably, the foam is a continuously extruded polyolefin foam that is substantially free of corrugation.

The article may comprise additional components that, when formed together with the article, form any of the following: athletic sports gear, buoyancy equipment, packaging cushion support, or specialty packaging case inserts for decorative display.

According to another aspect of the present invention, it provides a process of making the polyolefin foam, wherein the process comprises:

a) processing a resin blend of a base resin and a modifier resin, a permeability modifier, a nucleator, and a blowing agent in an extruder and a mixer at a temperature sufficient to melt the resin blend and to form a gel mixture,

b) uniformly cooling the gel mixture in a cooler to a predetermined foaming temperature, preferably, the predetermined foaming temperature is in the range of about 95-115°C, and

c) extruding the gel mixture through a die to form extruded foam at a predetermined pressure, preferably, in the range of above a prefoaming pressure that causes poor skin quality but below a predetermined pressure that causes corrugation. The process is a continuous extrusion process.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 illustrates the foaming temperature window of polyethylene (PE)/polyolefin plastomer (POP) foam formulations.

Figure 2 illustrates the foaming pressure window of PE/POP foam formulations.

Figure 3 illustrates the stress-strain behavior of PE & PE/POP foams.

Figure 4 illustrates the Shore A hardness of PE/POP, PE and crosslinked PE foams.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

In the following detailed description, the specific embodiments of the present invention are described in connection with its preferred embodiments. However, to the extent that the following description is specific to a particular embodiment or a particular use of the present techniques, it is intended to be illustrative only and merely provides a concise description of the exemplary embodiments. Accordingly, the invention is not limited to the specific embodiments described below, but rather; the invention includes all

alternatives, modifications, and equivalents falling within the true scope of the appended claims.

The technology detailed in the present invention involves the use of a modifier resin in the resin blend with a base resin, e.g. low density polyethylene (LDPE), to produce a polyolefin such as soft touch, fine cell size, and substantially closed cell polyolefin foam. Low density polyethylene (LDPE) is referred to as polyethylene having a density of about 0.915 to 0.930 g/cc, melting point of about 106 to 120°C and crystallinity of about 40 to 60%. The soft touch foam comprising the modifier resin and the base resin has superior elongational properties, improved soft feel characteristics, and good abrasion protection, especially for Class A surfaces. The technology covers the composition including resin and additive formulations and the process of foaming the soft touch foam.

A foam with a substantially closed cell usually contains about 80% or more closed cells or less than about 20% open cells according to ASTM D 2856-A. "Cell" refers to cavity contained in foam. A cell is closed when the cell membrane surrounding the cavity or enclosed opening is not ruptured and has all membranes intact.

It is discovered that the soft touch foam of the present invention has a desirably lower Shore A hardness. This feature indicates that the soft touch foam has a reduced material stiffness. The soft touch characteristic of the polyolefin foam is a qualitative attribute that is related to the cell size, initial compressive modulus, Shore A hardness and gloss retention during abrasion.

The soft touch foam of the present invention preferably has the following preferred characteristics with a density in the range of about 1.5-4 pound/cubic foot (pcf) (24-64 kg/m3), more preferably a foam with density of about 2 pcf (32 kg/m3):

- the cell size of the foam is preferred to be less than about 0.7 mm, more preferably less than about 0.6 mm,
- the initial compressive strength at 10% deflection is preferably less than about 5 psi (35 kPa),
- the Shore A hardness is preferably less than about 10,
- the gloss retention during abrasion preferably greater than about 0.975, more preferably greater than about 0.985.

The fine cell structure of the foam is important for achieving the soft feel characteristic and low abrasion performance. The fine cell foam preferably has a cell size less than about 0.7 mm and, preferably, less than about 0.6 mm. For a given cell size or density, the foam of the present invention shows excellent abrasion resistance for highly polished or painted Class A automotive surfaces.

The term "Class A surface" is used in automotive design to describe high finish surfaces of automobile parts that are visible to the customer and need to be aesthetically pleasing and free of nicks, dents, scratches and scuff marks.

The soft feel characteristics and low abrasion performance provide the foam with superior performance in protecting high quality automotive parts from nicks, dents, scratches and scuff marks during storage, handling and transportation from the OEMs (original equipment manufacturers) to the assembly plant. As a result, the foam is competitively advantaged over the existing materials in several high value applications, such as automotive parts protection, athletic sports gear, and buoyancy equipment.

The polyolefin foam of the present invention comprises a) a blend of a base resin and a modifier resin b) a permeability modifier, and c) a nucleator. Preferably, the foam is a non-crosslinked, substantially closed cell, soft touch foam. Because the inventive foam is not crosslinked, it is fully recyclable in an extruded foam process.

The base resin for the present invention may be low density polyethylene resin (LDPE) with moderate shear viscosity at low shear rates and adequate shear thinning behavior at high shear rates for good processability in an extrusion process line. The base resin preferably has broad molecular weight distribution (MWD) and long chain branching (LCB), which are desirable for good foamability.

The base resins of the present invention preferably have density in the range of about 0.915-0.930 g/cc, melting point in the range of about 106-120°C, and crystallinity in the range of about 40-60%. A preferred range for the melt index (ASTM D-1238) of the base resin is about 0.5-5 dg/min. The melt strength and drawability of the base resin are measured by the Rheotens™ melt tension apparatus and should be at least about 10 cN and 100 mm/s, respectively. The base resin makes up about 95-50% of the resin blend based on total weight of the base resin and modifier resin.

The modifier resin is important in the present invention. It ensures good foamability and processability of the formulation on the continuous extrusion process line to produce good quality foam with the desired properties.

In one preferred embodiment, the modifier resin may comprise substantially linear polymer of α-olefin polymers, for example, the substantially linear olefin polymers described in U. S. Patent Nos. 5,272,236 and 5,278,272, both incorporated herein by reference.

The substantially linear olefin polymers used in the present invention may be homopolymers of a C2-C20 α olefin, or preferably, interpolymers of ethylene with at least one C3-C20 α-olefin and/or a C4-C18 diolefin. These polymers contain a small amount of long-chain branching, about 0.01 to 3, preferably about 0.01-1, and more preferably about 0.3-1 long chain branch per 1000 carbon atoms. These polymers typically exhibit only a single melting peak by Differential Scanning Calorimetry (DSC).

The term "α-olefin" is used herein to indicate a polymer containing essentially no polymerized monovinylidene aromatic monomers and no sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers. Particularly suitable α-olefins have from about 2 to about 20 carbon atoms, preferably from about 2 to about 8 carbon atoms. Examples of the α-olefins may be ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene and the like. The preferred α-olefin polymers are homopolymers of ethylene and interpolymers of ethylene with a C_3-C_8 α-olefin.

The term "interpolymer" is used herein to indicate a polymer with at least two different monomers polymerized to make the interpolymer. This includes copolymers terpolymers, etc.

Particularly suitable substantially linear olefin polymers for the present invention preferably have a melt index (ASTM D 1238, Condition 190°C/2.16 kg) of from about 0.1 to about 100 dg/min, preferably from about 0.5 to about 5 dg/min, and a density of from about 0.850 to 0.970 g/cc, preferably about 0.850 to 0.950 g/cc, and more preferably about 0.850 to 0.920 g/cc. Examples of the substantially linear olefin polymers include polyolefin plastomers (POP) marketed by The Dow Chemical Company under the tradename Affinity™ or polyethylene elastomers (POE) under the tradename Engage™.

These unique polymers are prepared by using constrained geometry catalyst technology (CGCT) through controlled incorporation of low and high comonomer concentrations for plastomers and elastomers, respectively. According to "Classification of Homogeneous Ethylene-Octene Copolymers based on Comonomer Content" by S. Bensason, et. al., J. Appl Poly Sci, Part B Poly Physics, Vol 34, pg. 1301-1315, 1996 , the differentiation of the POP and POE is based on density and crystallinity and comonomer content (<20 wt % octene for Affinity™ polyethylene plastomers and >20 wt % octene for Engage™ polyethylene elastomers).

Suitable modifier resins used in the present invention may preferably be low modulus polyolefin plastomers (POP), such as ethylene-octene copolymers made by Dow constrained geometry catalyst technology (CGCT). These modifier resins have narrow molecular weight distribution (MWD), short chain branching (SCB) and controlled long chain branching (LCB). The modifier resins have lower melt strength, higher drawability and limited strain hardening compared to the base resins.

The term "low modulus" is used to describe resins with low crystallinity, preferably less than about 40%, and low density, preferably less than about 0.915 g/cc. A low modulus polyolefin plastomer with low crystallinity and low density has good flexibility and low stiffness.

The preferred POP resins have density in the range of about 0.860-0.910 g/cc, preferably about 0.885-0.905 g/cc, crystallinity in the range of about 25-35%, and contain about 10-20 weight % of octene comonomer. Resins from other suppliers that have the desired morphology and shear/extensional rheology may also be used. These resins bridge the gap between elastomers and plastic with rubber like properties and plastic processability. One of the preferred POP resins may be Affinity™, which is commercially available from The Dow Chemical Company.

The low modulus modifier resin makes up about 5-50% of the resin blend of the base resin and modifier resin. If the amount of the modifier resin is less than about 5-50%, the modulus reduction of the foam will be minimal. If the amount of the modifier resin is more than about 5-50%, the foamability of the foam will be affected.

The modifier resin of the present invention has narrow molecular weight distribution, short chain branching and controlled long chain branching. However, the use of this resin

alone for foaming is not practical because of its poor melt strength, high drawability and limited strain hardening compared to the base resin. The low crystallinity POP resin exhibits low storage modulus compared to the base resin.

It is discovered in the present invention that the use of the modifier resin in blends with the base resin such as LDPE results in improved softness and flexibility. According to the present invention, the base resin LDPE and the modifier resin POP blends exhibit a surprisingly synergistic response during extensional flow (e.g. foaming) with the blend having a higher melt strength than either of the individual resin components. The LDPE and the POP have crystallization temperatures that are well separated but the blend surprisingly exhibits a single Differential Scanning Calorimetry (DSC) crystallization temperature. The DSC crystallization temperature of the blend is close to that of the base resin. As a result, the foaming temperature of the LDPE/POP blend is close to that of the base resin LDPE, minimizing the risk of freeze-off of the base resin in the die or cooler during the foaming process. The melt index of the modifier resin is chosen to be close to that of the base resin to minimize viscosity mismatch concerns.

According to the present invention, the modified resin such as POP resin shows unexpected benefit for the soft touch performance. The POP resin can be foamed in a continuous extrusion process as the minor component in blends with a base resin such as LDPE as a major component without any additional processing issues, despite POP resin's lower crystallization temperature compared to the base resin. The POP resin as a component of the resin blend can also provide soft, substantially closed cell foams despite its low melt strength and limited strain hardening compared to the branched LDPE resin.

In addition to the blend of base resin and modifier resin, a permeability modifier, a nucleator and a blowing agent may be employed to the polymer blend formulation of the present invention.

The permeability modifier is added to the polymer blend formulation to enhance dimensional stability of the foam product. The preferred permeability modifier may be glycerol monostearate, which is commercially available under the trademark Atmer™ (available from Ciba). Other permeability modifiers may include stearamide, stearyl stearamide, glycerol di- and tri-stearate, glycerol mono and di-oleate, etc. The permeability modifier is employed in an amount of about 0.1-2.5, preferably about 0.1-1.5 parts per 100 parts polymer resin blend. Outside this range, the dimensional stability of the foam product

will be affected. An understabilized foam will be formed when the amount of the permeability modifier is lower than the range, and an overstabilized foam will be formed when the amount of the modifier is higher than the range.

The term "understabilized' is used herein to indicate a foam that suffers irreversible contraction during the aging process. The term "overstabilized" is used herein to indicate a foam that suffers irreversible expansion during the aging process. Both situations are undesirable as they result in foam with distorted cross-section and shape.

A nucleator, preferably a decomposable nucleator, is added to the foam formulation to regulate cell size within the foam. The preferred nucleator used in the present invention may be a mixture of citric acid/sodium bicarbonate, which is commercially available under the trademark Hydrocerol™ (available from Clariant). Other nucleators include talc, silica, or metal stearate such as calcium barium, zinc, and aluminum stearate, etc. may also be used. The nucleator is employed in an amount of about 0.1-4, preferably about 0.1-3 parts per 100 parts polymer resin blend. At levels lower than this range, minimal nucleation occurs. At levels higher than this range, no significant further effect on nucleation occurs as the additive primarily acts as a filler.

Blowing agents suitable for making the soft touch foams disclosed herein may be inorganic blowing agents, organic blowing agents, chemical blowing agents or a combination thereof. Examples of useful blowing agents are disclosed in US 6,720,363 B2, incorporated herein by reference. The blowing agent used in the present invention is preferred to be a hydrocarbon blowing agent. More preferably, the blowing agent is isobutane. The amount of the blowing agents used is dependent on the desired density of the foam and, in light of the disclosure herein, it is within the skill in the art to adjust this amount in order to achieve the desired density.

It is discovered in the present invention that the blend of the base resin and the modifier resin of the present invention, with a sufficient amount of the permeability modifier, the nucleator and the blowing agent, produces good quality, non-crosslinked fine cell, substantially closed cell, soft touch foam over a moderate foaming temperature range on a continuous extrusion process line.

The soft touch polyolefin foam is prepared by heating the polymer blend, additives including the modifier and the nucleator, and the blowing agent in an extruder and a mixer

at a temperature adequate to melt blend the feed, decomposing the nucleator and resulting in dispersed gas and solids. The gel mixture is then uniformly cooled to the desired foaming temperature in coolers. The foaming temperature may be in the range of about 95-115°C, more preferably in the range of about 100-110°C. The gel mixture can then be extruded or conveyed through a die of desired shape at a predetermined pressure above the prefoaming pressure which causes poor skin quality, but well below the pressure that causes corrugation. The prefoaming pressure may be about 400 psi (2758 kPa) and the pressure that causes corrugation may be about 900 psi (6205 kPa). The predetermined pressure is preferred to be in the range of about 400 psi (2758 kPa) to 900 psi (6205 kPa), more preferably in the range of about 450 psi (3103 kPa) to 850 psi (5861 kPa).

The mixer may be any of a variety of mixers, not limited to a second extruder, a static mixer, an interface surface generator, any of several varieties of rotary mixers including a rotating shaft in tube mixer, counter-rotating shafts in an elongated housing, a spline mixer, a cavity transfer mixer, and so on. The devices used for cooling the gel mixture may be any of a variety of coolers, including a second extruder, shell and tube cooler, tubular or plate type heat exchangers and the like. Also, the mixing and cooling operation can be combined in one step as with a second extruder, a cooled cavity transfer mixer and a cooled static mixer device.

A corrugated foam is a foam with surfaces (faces) that are not smooth and flat but are warped and folded into peaks and valleys. Corrugation, or folding of the foam, is usually caused by the rapid volumetric expansion rate of the small cells close to the die and the ease of expansion of the foam board in the extrusion and vertical directions relative to the difficulty in expansion in the horizontal (transverse) direction. i.e., due to the mismatch between the increase in the cross-sectional width of the board (occurs fast) relative to the horizontal spreading of the board (occurs slowly).

The process of this invention also includes an additional step to form the extruded foam using forming equipment such as rollers or belts close to the die. The forming assembly contacts the foam surface as it is extruded from the die and applies holdback (frictional force) to alter the horizontal blow-up ratio (HBUR= width of foam/width of die) and vertical blow-up ratio (VBUR= thickness of foam/die gap) and redirect the expansion from the width to the thickness (i.e. increase foam thickness at the expense of width) to improve flatness of the foam board.

The maximum processing temperature for making the foam should be about 180-200°C to obtain optimum gas yield and best nucleation efficiency from the dual mode nucleator.

The die pressure, as noted above, is selected to be above the prefoaming pressure that causes poor skin quality, (typically about 400 psi (2758 kPa) for 10% blowing agent in the formulation) and well below the pressure that causes corrugation (typically about 900 psi (6205 kPa) for 10% blowing agent in the formulation.

The conventional accumulating extrusion process used to make the fine cell foam is discontinuous. In this process, the polymer melt is extruded in a holding zone (accumulator) and periodically ejected by a movable ram out into ambient conditions where unrestrained foam expansion occurs. Unlike the accumulating extrusion process, the continuous extrusion process used in the present invention is capable of producing uniform fine cell foam having a flat profile that is substantially free of corrugation or without corrugation (wavy surface).

Foam with small cell size is important for achieving the soft feel characteristic and low abrasion performance. An elevated level of the permeability modifier (e.g. glycerol monostearate (GMS)), provides dimensional stability for fine cell foam with greater exposed cellular surface area for barrier layer coverage, but causes denucleation and cell size enlargement. The desired level of the permeability modifier in the formulation is a compromise between these competing effects. The permeability modification mechanism is believed to be due to migration of the permeability modifier to the polymer-air interface during foaming, due to its limited compatibility with the polymer, to form an ordered barrier structure. The ordered barrier structure reduces the diffusion of large molecular sized blowing agents, such as isobutane, out of the foam relative to the ingress of air and thereby minimizes excessive dimensional change of the foam board during the aging step.

Nucleation to achieve a foam with fine cell structure is provided by two routes: a) primary nucleation by a nucleator such as a mixture of citric acid and sodium bicarbonate that is effective at low-to-moderate loading but incrementally less effective at higher loading, b) Secondary nucleation by manipulating process conditions and die design (pressure drop and pressure drop rate at the die) so that the die pressure is above the prefoaming limit but sufficiently below the level that causes board corrugation. Operating below the prefoaming pressure results in foam with poor skin quality. Further improvement

in foam board flatness may be achieved by the use of forming devices close to the die that alter the blow-up, redirecting expansion from the width of the board to the thickness.

The polyolefin foam of the present invention may be competitively advantaged over the conventional materials in several valuable applications. The foam is very useful in automotive material handling, specialty packaging applications and as a key component in athletic sports gear and buoyancy devices. Possible applications may be for athletic sports gear such as hunting jackets, athletic pads and gym mats, buoyancy equipment such as life vests, personal flotation devices or protective cushion packaging of automotive parts with Class A surfaces. Further, the foam may also be used in specialty packaging applications, such as decorative displays and high end case inserts, where soft feel and high aesthetics are required.

The following examples and comparative examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

EXAMPLES

The following formulations are prepared to make fine cell, dimensionally stable non-crosslinked foam with about 2 pound per cubic foot (pcf) (32 kg/m3) density:

- 50-100 parts per hundred parts (pph) of low density polyethylene (LDPE) (XSS 84812.06 or PE620i) available from The Dow Chemical Company,
- 0-50 pph of polyolefin plastomer (POP) (Dow Affinity™ PL-1880) as the modifier resin available from The Dow Chemical Company,
- 0.5-2.5 pph 50% glycerol monostearate (GMS) (Atmer™ 7300) as the permeability modifier available as a concentrate in PE resin from Ciba Specialty Chemicals,
- 0.5-4 pph 20% mixture of citric acid/sodium bicarbonate (Hydrocerol™ CF-20) as the nucleator available as a concentrate in polyethylene (PE) resin from Clariant Additive Masterbatches, and
- 10 pph isobutane (iC4) as the blowing agent (BA) available from Airgas Inc.

The additives including the permeability modifier and the nucleator are present as parts per hundred parts (pph) of total polymer resins. The blowing agent is present as parts per hundred parts solids feed (including resins and additives).

The resin properties are summarized below:

- PE620i: melt index: 1.8 dg/min,
  density: 0.924 g/cc,
  Differential Scanning Calorimetry (DSC) crystallization temperature: 97°C,
  DSC heat of crystallization: 82 J/g,
  storage modulus, G': 8.9,
  melt strength: 14 cN,
  drawability: 200 mm/s.
- XSS84812.06:
  melt index: 0.88 dg/min,
  density: 0.923 g/cc,
  melt strength: 15 cN,
  drawability: 180 mm/s.
- PL-1880:
  melt index: 1.0 dg/min,
  density: 0.902 g/cc,
  DSC crystallization temperature: 81°C,
  DSC heat of crystallization: 53 J/g,
  storage modulus G': 2.4,
  melt strength: 5 cN,
  drawability: 275 mm/s.

The melt index is determined using ASTM D 1238. The melt strength and drawability are determined by Rheotens™ melt indexer, the density is determined by ASTM D 792, crystallization temperature and heat of crystallization are determined by Differential Scanning Calorimetry (DSC) (ASTM D 3417/3418).

A pilot extrusion process line used for making the foam includes the following equipment:

- resin and additive feeders and a single screw extruder used to melt, mix and forward the resin and additives;

- a mixer used to disperse the blowing agent into the melt, with an optional gear pump to provide consistent feed rate and dampen pressure fluctuations;
- Coolers are used to uniformly cool the polymer resins, additives and blowing agent mixture to the foaming temperature; and
- a die with an adjustable slit is used to shape the extrudate as it emerges from the pressurized line to ambient conditions, facilitating the expansion of the foam to the desired profile and stabilization of the foam structure by external air cooling with fans or blowers.

The resins and solid additives are added from gravimetric or volumetric feeders to the feed throat of the extruder in starve feed mode. The blowing agent and liquid additives are fed to the mixer via positive displacement pumps. The line is run at about 40 lb/hr (residence time of about 15 min) using a ½" or 1" wide adjustable die and is controlled with a process control system. After a formulation change is made, the line is allowed to stabilize for at least three residence times before a representative sample is taken.

For the Polyethylene (PE)/Polyolefin Elastomer (POP) blend foam, the following extruder temperature profile is used:

- feed zone set at about 120°C;
- transition zone at about 140°C;
- melt zone at about 165°C; and
- metering zone at about 180°C.

The mixer is set at about 180°C. The maximum gel temperature in the extrusion line, at the extruder outlet (about 200°C), is higher than the metering zone set-point (about 180°C) due to shear heating.

The maximum pressure is at the mixer outlet (about 3200 psi or 22060 kPa) after blowing agent addition. The heat transfer fluid temperature set-points for the coolers are adjusted so that the temperature of the gel entering the die is between about 95°C and 115°C.

The temperature set point of the cooler and die body are adjusted to make good quality foam. The die pressure is maintained above the prefoaming limit that causes poor

skin quality (about 400 psi, 2758 kPa) and below the pressure that causes corrugation (about 900 psi, 6205 kPa) by adjusting the die opening.

Example I - Foaming Temperature Window

The foaming temperature window is the temperature range of the polymer resins/additive/blowing agent mixture at the die that results in stable foam with the lowest density and open cell content less than about 20%. Above the temperature range specified, the foam has generally poor stability, high open cell content (> about 25%) and collapses. Below the temperature range, the polymer crystallizes out of the melt and freezes in the die and cooler, resulting in poor heat transfer.

The foaming temperature window of a formulation in the foam extrusion process is experimentally determined by changing the cooler and die body temperatures in step-wise fashion while monitoring the die pressure, the density, open cell content and foam quality.

The foam samples designated 60/40 PE/POP in Figure 1 are made with the following formulation:

- resin blend: 60/40 polyethylene (PE) XSS 84812.06/polyolefin plastomer (POP) PL-1880;
- permeability modifier: 1.5 pph GMS;
- nucleator: 1.5 pph CF-20; and
- blowing agent: 10 pph iC4.

For the foam samples designated 60/40 PE/POP, the results in Figure 1 indicate a foaming temperature range of 102-105°C and a foaming temperature window, $\Delta T_{foaming}$, of 3°C for producing dimensionally stable foam with open cell content below 20%.

The foaming temperature window obtained experimentally on a pilot scale line is moderately broad and is believed to be adequate for scaling purposes to make good quality foam on a large scale production line. The die pressure for the foam formulations is ranged between about 420 and 462 psi (2896-3185 kPa). The density of all the foams is ranged between about 1.9-2.1 pcf (30-34 kg/m^3). All the foam products exhibit good skin quality with no corrugation or folding. The results show that for the 60/40 PE/POP formulation, the continuous extrusion process of the invention can be used to make good quality,

corrugation free, substantially closed cell foam with a foaming temperature preferably in the range of 102-105°C and a moderately broad foaming temperature window of 3°C.

The samples designated 50/50 PE/POP in Figure 1 are made with the following formulation:

- resin blend: 50/50 polyethylene (PE) XSS 84812.06/polyolefin plastomer (POP) PL-1880;
- permeability modifier: 2.0 pph GMS;
- nucleator: 1.5 pph CF-20; and
- blowing agent: 10 pph iC4.

For the foam samples designated 50/50 PE/POP, the results in Figure 1 indicate a foaming temperature range of 100-102°C and a foaming temperature window, $\Delta T_{foaming}$, of 2°C for producing dimensionally stable foam with open cell content below 20%. The foaming temperature window obtained experimentally on a pilot scale line is moderately broad and is believed to be adequate for scaling purposes to make good quality foam on a large scale production line. The die pressure for the foam formulations is ranged between 444 and 455 psi (3061-3137 kPa). The density of all the foams is ranged between 1.9-2.0 pcf (30-32 kg/m3). All the foams exhibited good skin quality with no corrugation or folding. The results show that for the 50/50 PE/POP formulation, the continuous extrusion process of the invention can be used to make good quality, corrugation free, substantially closed cell foam with a foaming temperature preferably in the range of 100-102°C and a moderately broad foaming temperature window of 2°C.

Additional experiments also show that for 95/5 PE/POP to 50/50 PE/POP formulations, the continuous extrusion process of the invention can be used to make good quality, corrugation free, substantially closed cell foam with a foaming temperature in the range of 95 to 115°C and, more preferably, in the range of 100-110°C.

These results are unexpected because the crystallization temperatures of the LDPE and POP resins in the foam formulation are widely separated. In a conventional extrusion process, when a foaming temperature is close to that of the crystallization temperature of the base resin, the modifier resin remains in a molten state for an extended period of time as the

foam expands and as the base resin crystallizes. As a result, weak spots are believed to be induced that cause ruptures in the cell wall leading to the formation of open cell foam.

These results are also especially unexpected because of the low melt strength and poor strain hardening characteristics of the POP resin. Resins with the abovementioned rheological (shear or extensional flow) properties and blends containing such resins usually are very difficult to foam and produce stable closed cellular structures.

Example II - Foaming Pressure Window

The lower limit of the operating pressure range is the pressure at which prefoaming occurs, which is the minimum die pressure to maintain the blowing agent solubilized in the melt. At pressures below the prefoaming pressure, premature release of the blowing agent occurs with degassing at the die, evidenced by a crackling sound, and results in a poor quality foam with very rough skin due to the rupture of surface cells.

The upper limit of the operating pressure range is the pressure at which corrugation occurs. Corrugation or folding is caused by the uneven directional expansion of the gas for a given die take-up configuration resulting in a wavy or warped profile rather than the desired smooth flat surface. Corrugation occurs due to the ease of expansion in the vertical and extrusion directions accompanied by the difficulty in expansion in the horizontal direction, especially in the presence of higher levels of blowing agent necessary to attain lower density.

The samples in Figure 2 are made with the following formulation:

- resin blend: 60/40 polyethylene (PE) XSS 84812.06/polyolefin plastomer (POP) PL-1880;
- permeability modifier: 1.25 pph GMS;
- nucleator: 1.5 pph CF-20; and
- blowing agent: 10 pph iC4.

The exit temperature from the cooler and die temperature are maintained at 107°C and the die pressure is varied between 400 and 900 psi (2758 - 6205 kPa) by changing the die opening of the adjustable slit die in a step-wise fashion and noting the quality of the foam skin and board profile. As the die opening is reduced for a given throughput rate, the

cross-sectional area of the die decreases resulting in a decrease in foam thickness and an increase in the linear speed of foam exiting the die.

The results, presented in Figure 2, show that the prefoaming pressure for the formulation of the invention is about 400 psi (2758 kPa). At pressures below this pressure, the quality of the skin deteriorates significantly due to rupture of the surface cells and a crackling sound is audible due to the degassing of the blowing agent at the die.

The results also show that the corrugation pressure for the formulation of the invention is about 900 psi (6205 kPa). At pressures above this pressure, the quality of the board deteriorates significantly due to the die induced nucleation and the faster expansion rate in the extrusion and vertical directions relative to the horizontal (or cross) direction resulting in a corrugated profile with peaks and valleys rather than a flat board.

The results show that the continuous extrusion process of the invention can be used to produce foam boards free of corrugation and with good skin quality by operating at die pressures above 400 psi (2758 kPa) and below 900 psi (6205 kPa).

Example III - Stress-Strain Behavior of the Foams

The use of a modifier resin in blends with low density polyethylene is important to achieve a reduction in modulus resulting in softer foam. The stress (force per unit area) and strain (ratio of change in length per original length) are recorded as the foam is compressed by a universal testing machine (e.g. Instron^{TM}). The modulus is the ratio of stress to strain over the linear (elastic) range and is obtained from the initial slope of the stress vs. strain curve. As the modulus decreases, the compressive strength (stress) of the foam for a given deflection (strain) decreases.

The samples in Figure 3 denoted as PE/POP are prepared using the following formulations at a foaming temperature of 102°C and a die pressure of 438 – 463 psi (3020 – 3192 kPa):

- resin blend: polyethylene (PE) XSS 84812.06/polyolefin plastomer (POP) PL-1880, with blend ratios varying from 80/20 to 60/40;
- permeability modifier: 2.5 pph GMS;
- nucleator: 4.0 pph CF-20; and
- blowing agent: 10 pph iC4.

The sample in Figure 3 denoted as PE is prepared using the following formulation at a foaming temperature of 105°C and a die pressure of 409 psi (2820 kPa):

- PE XSS 84812.06
- permeability modifier: 2.0 pph GMS,
- nucleator: 4.0 pph CF-20, and
- blowing agent: 10 pph iC4.

Incorporation of the POP resin in the PE foam formulation results in a decrease in the modulus of the foam and an increase in the elongational properties as shown in Figure 3. For example, at a deflection of 10%, the compressive strength of the PE/POP foams ranged between 2.3 to 4.6 psi (16 to 32 kPa) whereas the compressive strength of the PE foam was 7.1 psi (49 kPa). The modulus is the slope of the stress-strain curve and visual observation of the curves shows that the modulus of the PE/POP foams is less than that of the PE foam. The PE/POP foams exhibit a compressive strength of less than about 5 psi (35 kPa) at 10% deflection. These foams exhibit good skin quality and are free of corrugation.

Example IV - Shore A Hardness of the Foams

Incorporation of POP resin in the PE foam formulation results in a softer foam and a decrease in the resistance of the foam to penetration by an indenter as determined by the Shore A durometer. The Shore A hardness on a scale of 0-100 can be used as an indicator of foam stiffness, with lower Shore A values corresponding to less resistance to indentation.

Incorporation of the POP resin in the PE foam formulation results in a decrease in the resistance to indentation of the foam as shown in Figure 4. For example, 60/40 PE/POP foams have a Shore A hardness ranging between 4.3 and 6.6 with an average Shore A hardness of 5.7. Figure 4 also shows that 70/30 PE/POP foams have a Shore A hardness ranging between 6.1 and 6.7 with an average Shore A hardness of 6.4. Figure 4 also shows that PE foams have a Shore A hardness ranging between 10.2 and 14.9 with an average Shore A hardness of 11.7. A commercial crosslinked foam used in Class A automotive material handling applications with very fine cells has a Shore A hardness of 8.7. However, it is not recyclable and does not meet the new environmentally driven market needs. The PE/POP foams in Figure 4 exhibit a Shore A hardness of less than about 10. These foams exhibit good skin quality and are free of corrugation.

Example V – Abrasion Performance of the Foams

Incorporation of the POP resin in the PE foam formulation produces a foam with superior abrasion performance. The abrasion performance of the foam on a high gloss substrate is determined with a modified ASTM D 5264 procedure using a Sutherland 2000 abrasion tester. A 4" x 2" x 2.125" foam sample is skived to remove the skin and inserted into the sample holder of the rubbing arm with the desired static load. The test surface is a high gloss painted automotive metal plaque. Prior to the test, the gloss of the test surface is measured at three points with a gloss meter at 20° and 60° angles and the average initial gloss before testing is calculated. The rubbing arm is lowered to contact the metal plaque and the skived foam is rubbed against the high gloss painted metal plaque under a given load and predetermined speed for a fixed number of cycles. After the test is complete, the gloss of the test surface is remeasured at the same three points at 20° and 60° angles and the average final gloss after testing is calculated. The ratio of the average final gloss to the average initial gloss is determined and its value on a scale of 0 to 1 is an indicator of foam abrasivity for Class A automotive surfaces (i.e. Gloss retention = Average final gloss after testing / Average initial gloss before testing).

A gloss retention of greater than 0.975, preferably greater than 0.985, is desirable for low abrasion performance in use. The abraded plaque is also visually rated on a qualitative scale of 0-5 for the level of scratches, marks or haze. The results of abrasion testing of several foam samples of the invention and comparative foam samples are presented in Table I below. The quantitative results of the change in gloss of the surface of the substrate after abrasion with the foam measured with a gloss meter and the qualitative results by visual observation are provided.

The sample labeled Ex. 1 in Table I is prepared using the following formulation at a foaming temperature of 104°C and a die pressure of 441 psi (3040 kPa) to make a corrugation-free foam with good skin:

- 60/40 blend of PE XSS 84812.06 and POP Affinity PL-1880;
- permeability modifier: 2.0 pph GMS;
- nucleator: 2.0 pph CF-20; and
- blowing agent: 10 pph iC4.

The sample labeled Ex. 2 in Table I is prepared using the following formulation at a foaming temperature of 102°C and a die pressure of 451 psi (3110 kPa) to make a corrugation-free foam with good skin:

- 80/20 blend of PE XSS 84812.06 and POP Affinity PL-1880;
- permeability modifier: 2.5 pph GMS;
- nucleator: 4.0 pph CF-20; and
- blowing agent: 10 pph iC4.

In Table I, samples Ex. 1 and Ex. 2 are examples of the present invention. The samples designated Comp Ex. 1 and Comp Ex. 2 are comparative samples and represent the commercially available non-crosslinked Synergy™ 1000 foam and Ethafoam™ 220 foam, respectively. These commercially available foams are made with LDPE only.

The results in Table I show that cell size is an important parameter that impacts the abrasion performance of the foam. As the cell size of PE foam is decreased, the average gloss retention increases (compare Ex. 1 and Ex. 2, Comp Ex. 1 and Comp Ex. 2). The results confirm that the PE/POP foams show low abrasion performance of fine cell foam and the benefits of using a soft low modulus POP resin in the foam formulation in conjunction with the base PE resin. Crosslinked foams with good abrasion performance are used as packaging material for the protection of automotive parts with Class A surfaces during transportation but are not recyclable. The foams of the invention are 100% recyclable, meeting the new environmentally driven market needs and also provide the desired performance for the Class A automotive material handling application.

Table I: PE & PE/POP Foam Properties and Performance

Sample	Resin Blend	Cell Size, mm	Density, pcf	Open Cell Content, %	Compressive strength @ 10% deflection, psi	Shore A hardness	Avg. Gloss Retention	Abrasion Scale (visual)
Ex. 1	60/40 PE/POP	0.64	1.9 (30 kg/m3)	18	2.4 (17 kPa)	5.6	0.983	1.5
Ex. 2	80/20 PE/POP	0.59	2.1 (34 kg/m3)	12	4.6 (32 kPa)	6.9	0.987	1
Comp Ex. 1	PE	0.85	1.8 (29 kg/m3)	9	6.2 (43 kPa)	11.3	0.970	2
Comp. Ex. 2	PE	1.3	2.2 (35 kg/m3)	7	7.1 (49 kPa)	12.4	0.960	3

Abrasion test conditions: Speed: 4, Rub Count: 25, Static Load: 0.136 psi (0.9 kPa)
Abrasion Scale:

1. Zero to miniscule marks on plaque.
2. Slight marking on test plaque.
3. Small amount of light scratches or marks.
4. Significant scratches or marks.
5. Heavy scratches or marks.

The soft feel or soft touch attribute desired in the foam is a human tactile response that is difficult to simulate or characterize with test equipment. The softness of the foam, as measured by human touch, is a qualitative attribute that can be related to foam properties, such as cell size, and foam attributes and performance indicators, such as initial compressive modulus, Shore A hardness and gloss retention during abrasion. For a foam with density of about 1.5 to 4 pcf (24-64 kg/m3), preferably about 2 pcf (32 kg/m3) foam, the cell size is preferably less than about 0.7 mm, more preferably less than about 0.6 mm, the initial compressive strength at 10% deflection is preferably less than about 5 psi (35 kPa), the Shore A hardness is preferably less than about 10, and the gloss retention during abrasion is preferably greater than about 0.975, more preferably greater than about 0.985.

It will be obvious to persons skilled in the art that certain changes may be made in the methods described above without departing from the scope of the invention. It is therefore intended that all matter herein disclosed be interpreted as illustrative only and not as limiting the scope of protection sought. Moreover, the process of the present invention is not to be limited by the specific examples set forth above including the tables to which they refer. Rather, these examples and the tables they refer to are illustrative of the process of the invention.

CLAIMS:

1. A continuously extruded non-crosslinked polyolefin foam comprising:

a) a resin blend of a base resin and a modifier resin,

b) a permeability modifier, and

c) a nucleator,

wherein the base resin comprises a low density polyethylene (LDPE) and the modifier resin comprises a substantially linear polymer of α-olefin, and wherein the foam is substantially free of corrugation.

2. The foam according to claim 1, wherein the substantially linear polymer of α-olefin comprises a homopolymer of a C_2-C_{20} α-olefin or an interpolymer with at least one C_3-C_{20} α-olefin and/or a C_4-C_{18} diolefin.

3. The foam according to claim 1, wherein the low modulus polyolefin plastomer (POP) has a density in the range of about 0.860 to about 0.910 g/cc.

4. The foam according to claim 1, wherein the base resin has a density in the range of about 0.915 to about 0.930 g/cc and crystallinity of about 40 to about 60%.

5. The foam according to claim 1, wherein the base resin and the modifier resin have a melt index from about 0.50 to about 5.0 dg/min.

6. The foam according to claim 1 comprising fine cells with substantially closed cell structure.

7. The foam according to claim 1, wherein the resin blend comprises about 95-50 wt. % of the base resin and about 5-50 wt. % of the modifier resin.

8. The foam according to claim 1, wherein the permeability modifier comprises at least one of glycerol monostearate, stearamide, stearyl stearamide, glycerol di- and tri-stearate, glycerol mono, di-oleate, or a mixture thereof.

9. The foam according to claim 1, wherein the nucleator comprises a mixture of citric acid and sodium bicarbonate, talc, silica or metal stearate.

10. The foam according to claim 1 having a density of about 1.5 to 4 pcf (24 to 64 kg/m3).

11. The foam according to claim 10 comprising fine cells, wherein the fine cells have a cell size of less than about 0.7 mm, and wherein the foam has at least one of the following properties: an initial compressive strength at 10 % deflection of less than about 5 psi (35 kPa); a Shore A hardness of less than about 10; or a gloss retention during abrasion of greater than about 0.975.

12. An article comprising a continuously extruded non-crosslinked polyolefin foam, wherein the foam comprises:

a) a resin blend of a base resin and a modifier resin,

b) a permeability modifier, and

c) a nucleator,

wherein the base resin comprises a low density polyethylene (LDPE) and the modifier resin comprises a substantially linear polymer of α-olefin, and wherein the foam is substantially free of corrugation.

13. The article according to claim 12 further comprising additional components forming in combination with any one of the following: athletic sports gear, buoyancy equipment, packaging cushion support, or decorative display.

14. The article according to claim 13 wherein the packaging cushion support is for an automotive part with a Class A surface.

15. A process of making a non-crosslinked polyolefin foam comprising:

a) processing a resin blend of a base resin and a modifier resin, a permeability modifier, a nucleator, and a blowing agent in an extruder and a mixer at a temperature sufficient to melt the resin blend and to form a gel mixture;

b) uniformly cooling the gel mixture in a cooler or a series of coolers to a predetermined foaming temperature;

c) extruding the gel mixture through a die using a continuous extrusion process to form an extruded foam at a predetermined pressure; and

d) forming the extruded foam using a roller or belt close to the die to alter the blow-up ratio and redirect the expansion of the foam from the width to the thickness to improve flatness of the foam.

16. The process according to claim 15, wherein the predetermined foaming temperature in b) is in the range of about 95-115°C.

17. The process according to claim 15, wherein the predetermined pressure in c) is in the range of above a prefoaming pressure that causes poor skin quality but below a predetermined pressure that causes foam corrugation.

18. The process according to claim 17, wherein the predetermined pressure in c) is in the range of about 400 psi (2758 kPa) to 900 psi (6205 kPa).

19. The process according to claim 15, wherein the base resin comprises a low density polyethylene (LDPE) and the modifier resin comprises a substantially linear polymer of α-olefin, and wherein the foam is substantially free of corrugation.

20. A non-crosslinked polyolefin foam made by the process of any one of the claims 15 to 19 comprising:

a) a resin blend of a base resin and a modifier resin,

b) a permeability modifier, and

c) a nucleator,

wherein the base resin comprises a low density polyethylene (LDPE) and the modifier resin comprises a substantially linear polymer of α-olefin, and wherein the foam is substantially free of corrugation.

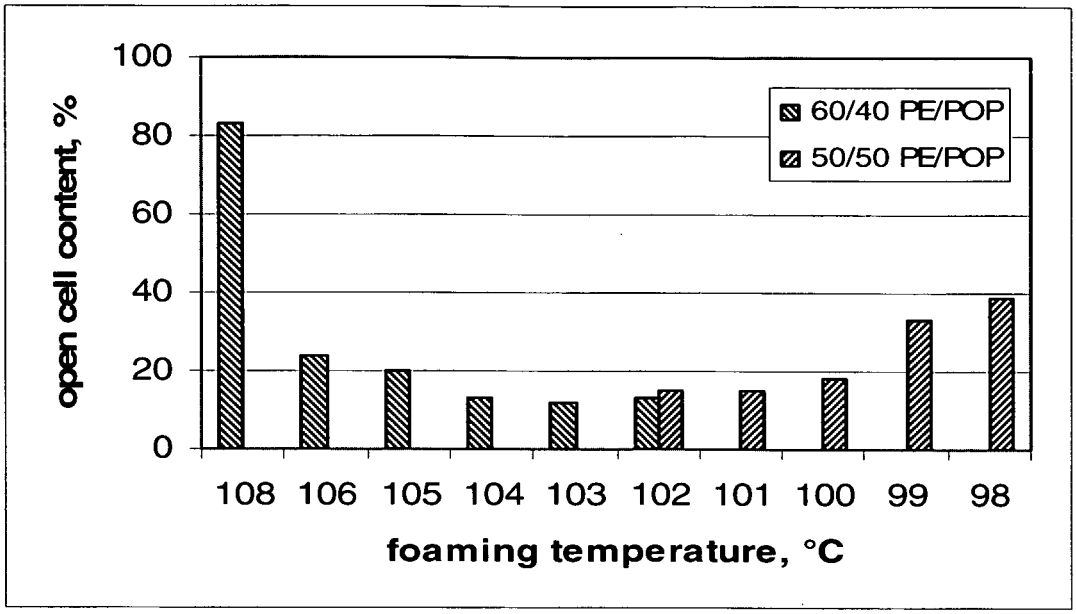

Figure 1: Foaming Temperature Window of PE/POP Formulations

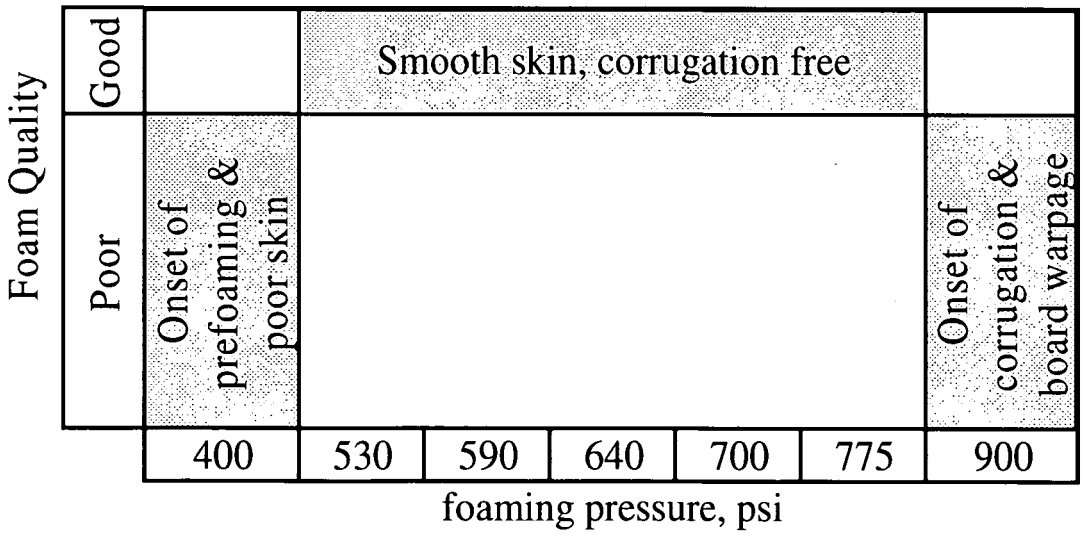

Figure 2: Foaming Pressure Window of PE/POP Formulations

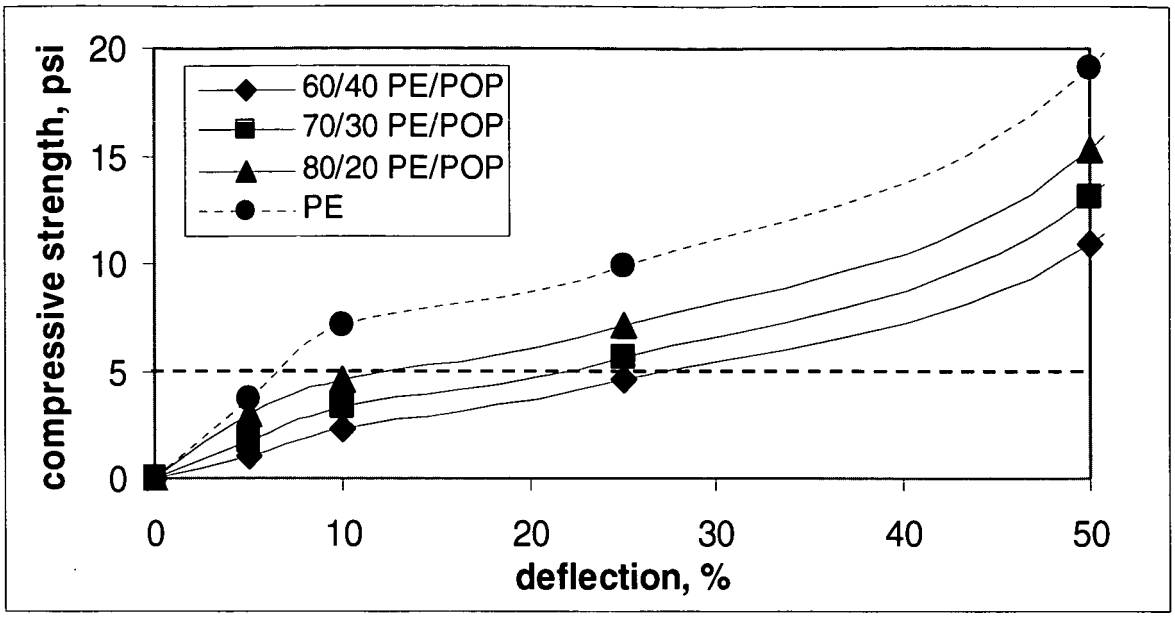

Figure 3: Stress-Strain Behavior of PE & PE/POP Foams

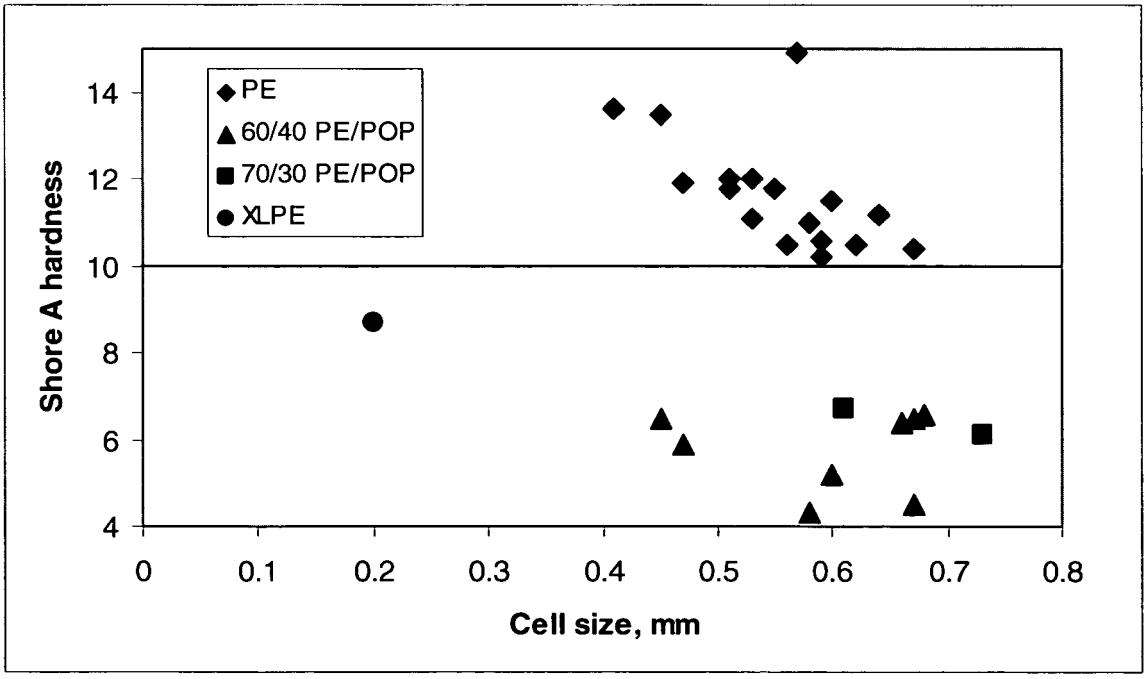

Figure 4: Shore A Hardness of PE/POP, PE & XLPE Foams