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Manufacturing Open-Cell Soft Thermoplastic Foams for Personal Devices: A Literature Review and Recommended Research Proposal

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1. Introduction

Kimberly-Clark Corporation (KCC) is a world leader in personal hygiene products such as tissue, personal protection, medical products, and diapers. These products require fluid absorbing properties, softness, flexibility, and need to be suitable for direct contact with the human body. For many applications, elasticity is desired. These properties are now met generally with wood fibres, polypropylene (PP) and thermoplastic elastomeric fibres, and polyolefin films but Kimberly-Clark is evaluating other ways to obtain such properties. For instance, soft thermoplastic absorbent foams might possess the needed performance requirements.

Foams suitable for disposable and absorbing devices should have an open-cell morphology, a density lower than 100 kg/m^3 (preferably lower than 50 kg/m^3), and be soft, flexible, resilient, and low-cost. Biodegradability is also desired. A more complete set of specifications that was provided by KCC is reported in Table 1. NRC agreed to help KCC in evaluating the potential of foams for their products. In addition to joining FoamTech, KCC asked NRC to gather pertinent information on material properties and evaluate the feasibility of using foams. Should the results prove promising, KCC maybe interested in collaborating further with NRC to validate a few of the ideas.

Table 1: Foam Material Specifications

Property	Description
Absorbency	
Durable wettability	Maintain wettability with multiple fluid additions. Surfactant does not substantially wash off.
Capacity	Low density (< 0.1g/cc) to ensure sufficient capacity – 30x expansion.
Wicking	Move liquid against gravity at a rapid rate.
Mechanical/Physical	
Open Cell Content	Well-connected cell structure to maximize space utilization (>80% open-cell).
Thickness	Thickness (<3-4mm)
Stiffness	Flexible and conformable – cloth-like
Softness/hand	Soft
Compression Resistance and set	Highly resilient – minimal set after high level of compression
Stability to aging	Withstand transportation and warehouse conditions and have good shelf life
Safety	Personal care standards
Cost	
Polymer + additives used	≤ $2.50/lb

2. Literature Review

An on-line literature review was conducted using thirteen different databases. Both scientific and patent titles were obtained. The research was conducted using a combination of concepts that focused on low-density open-cell flexible foams made from thermoplastic materials. See Annex A and Table A-1 for the detailed search strategies used to combine these different concepts. The lists of the selected patents used for this review and pertinent comments are given in Tables B-1 and B-2.

By combining concepts, 34 different titles were obtained from which, 12 complete references were selected. Moreover, other references were obtained by performing in-house searches on *Current Contents* and *El Compendex*, and by using textbooks, FoamTech materials, US Patents, and other sources previously available. Not all selected references were found relevant to the scope sought by Kimberly-Clark. Most of the open-cell flexible foams found in the literature are made of thermoset polyurethanes. Still, there are a few patents and articles disclosing the fabrication of soft and/or open-cell thermoplastic foams.

An early patent published in 1970 [1] describes the formulation of a free-rising open-cell foam made from polyethylene and ethylene-alkyl acrylate polymers and was expanded with a chemical blowing agent and then cross-linked with dicumyl peroxide. Optionally, a low viscosity silicone additive could be used to control foam nucleation. Although chemical blowing agents and cross-linking agents are not suitable for the application sought by Kimberly-Clark, there is evidence from this particular patent that open-cell low-density foams (as low as 2.2 pounds per cubic foot or 35 kg/m^3) can be obtained with the aforementioned thermoplastic resins. The open-cell foams have utility for furniture upholstery, cushioning, and fabrication of sporting equipment.

In another invention, Shikinami et al. [2] disclosed the production of open-cell thermoplastic foams using a cross-linked polymer blend comprised of a polyolefin, a vinyl copolymer, or a butadiene copolymer, and expanded with a chemical blowing agent. The inventors claim that success in the production of the open-cell structure lies in the formation of a partially cross-linked thermoplastic network that is able to sustain excessive deformation and thus allows the rupturing of the cell walls without contraction of the cell struts.

Ladang and Petit [3] disclosed a formula for making soft flexible closed-cell polyolefin foam. The particularity of the invention is that the polyolefin is partially cross-linked, preferably with a 45-55% gel fraction, to produce a low-density foam sheet. A similar invention is described by Sueda et al.[4] where an elastomeric foam is expanded to low densities. Again, the composition is cross-linked with organic peroxide.

Flexible closed-cell foams, without using cross-linking agents, were produced by blending styrene-elastomer block copolymer and polyolefin. Linear tri-block SEBS copolymers are sold under the trade name *Kraton G* series copolymers by Kraton Polymers or the *Septon* series by Kuraray America [5]. The blend is expanded with a volatile organic liquid or a chemical blowing agent. Additionally, plasticizing oil can be added to improve flexibility, as well as other additives commonly used for imparting specific functionalities (UV stabilizers, fillers, pigments, antioxidants, etc.). The inventors state that the preferred SEBS block copolymer used in the invention does not melt, but can be melt processed once it is blended with polyolefins.

Ethylene vinyl acetate (EVA) can also be used to produce low-density flexible foams. Rodríguez-Pérez and de Saja [6] studied the impact of blending EVA or polyisoprene-polystyrene block copolymer (IS) with LDPE. EVA, in comparison to LDPE, is more flexible and find uses in many applications such as: insoles, mats, body protection items, etc. IS has excellent dampening properties and reduces the stiffness of foam. The density of the foam samples tested ranged between 45-80 kg/m^3.

Kim and Kim [7] showed that it is possible to control the fraction of open cells by radiation cross-linking LDPE and EVA foams. The authors concluded that a small proportion of gel (about 25%) produced slightly higher open-cell contents. They concluded that greater melt strengths could prevent cell collapse while allowing cellular interconnection; however, non-cross-linked EVA and LDPE foams still contained open cells.

A patent describing a wound dressing contains interesting information regarding open-cell foams having absorbent properties [8]. The background of the invention indicates that absorbency will be highly dictated by the cell size and morphology. Suitable open-cell hydrophilic foams should preferably have cell sizes between 50 and 500 microns. Moreover, the preferred open-cell fraction should range between 30% and 60%. Though the open-cell conformable foam described in the invention is made of polyurethane, the preferred morphological requirements should also apply to foam made from thermoplastic polymers.

The Dow Chemical Company applied for a world-wide patent describing formulations for producing absorbent thermoplastic foams that can be used in diapers or meat trays [9-10]. The patent covers much of the common thermoplastic polymers (without any regard to flexibility) and blowing agents known in the state of the art. Additionally, the inventors claim that adding a minor amount of a polymer different from the predominant polymer enhances open-cell formation. The morphology of the open cells is critical to a foam's performance. The inventors observed that the fastest fluid wicking rates were obtained from foams having an average cell size of 70 µm. These findings are in agreement with those obtained by Lang and Webster [8]. Moreover, elongating cells in the extrusion direction improved wicking rates. Absorbency can be further improved by adding surfactant on the foam's surface.

Multiple patents claim that blending immiscible polymers together increases a foam's open-cell content. The approach generally involves blending amorphous components with semi-crystalline polymers. Blends of atactic (amorphous) PP with crosslinkable resins, such as LDPE, HDPE and EVA, are among the first cases described in patents that utilize this idea [11]. The inventors claim crosslinked foams can be fabricated having uniform cell sizes, open-cell contents greater than 40%, but relatively modest expansion ratios of 7 to 8. Other examples include blends of polybutadiene with either polyolefins or vinyl polymers [12], polyolefins with styrene or methacrylic polymers [13], and ethylene polymers with either EVA [14-17] or polysiloxane [18]. In a detailed formulation-based patent, Kogure et al. extensively describe the use of ionomers and rubbery materials (EPR, LLDPE, styrenic elastomers) for fabricating open-cell foams for cushioning and packaging applications. [19] The inventors claim a greater than 50% open-cell content with a foam density ranging between 15 and 200 kg/m^3. Examples of numerous patents based on the modification on PS with ethylene-based polymers can be found in References [20, 21]. Large increases in open-cell content (up to 95%) are reported when blending PE (or EVA, EEA, EBA...) with PS prior to foaming. Details of

these examples and other cases are reported in Tables B-1 and B-2. Patent literature briefly proposed the possible mechanism leading to open-cell generation for blends of immiscible polymers [22]. Elaborating on the mechanism, it seems reasonable to assume a reduction in melt extensibility upon addition of immiscible domains within the base polymer matrix material. These immiscible domains would act as defects and induce cell wall rupture during the expansion stage. With the cell window vibration that Colton proposes [23], these weak areas of defect more readily rupture forming a cell opening that connects adjacent cells. Blending the different polymers prior to foaming appears to be the universal method to enhance open-cell content in foams. Using elevated melt temperatures in the foaming process is also commonly used to control open-cell content (this will be explored in greater details in a further section).

A surfactant was also added to improve the absorbency of trays described in the invention of Lanzani and Mauri [24]. These trays are made of an expanded open-cell polymer sheet comprised of polystyrene, polyvinyl chloride, and their copolymers. To provide absorbency, holes are produced at the surface of the foam to allow liquid penetration into the foam structure. Following on that idea, two patents describe the use of a mechanical treatment to induce/increase the open-cell content. Extrudate elongation is applied to the melt exiting the die as described in Reference [10] to *"assist pore formation and open-cell formation."* Similarly, mechanical compression, as described in Reference [25], is utilized to rupture cell membranes and increase open-cell content. These approaches are based on using mechanical stresses on foam to induce larger open-cell content and at first might seem appealing. However, information mentioned in Reference [26] points out that open cells created by mechanical action leave cell wall residues that lead to reduction in foam water absorption capability. Caution should be taken in selecting mechanical treatment technique(s) to minimize the amount of cell wall remnants left imbedded in the foam. Methods applied during the expansion stage versus post-treatment methods done on solidified foams (mechanical punctures and the like) are therefore preferred.

Rodeheaver and Colton proposed a theory for generating open-cell microcellular polystyrene foams [23]. Although foams required by Kimberly-Clark are not microcellular, some theoretical aspects remain the same. According to the authors, the formation of open cells follows two stages: the impingement of the bubbles and the rupture of the thin film between two adjacent bubbles. For impingement to occur, nucleate cell density (the number of bubbles per volume) has to be sufficiently high enough which indicates that a critical nucleation density exists. Second, the thin walls between the cells must break spontaneously. In the latter stage, the viscosity of the polymer matrix will determine its resistance to deformation.

At last we should mention the review of various cell opening mechanisms proposed for aqueous foam and flexible polyurethane (PU) foam [27]. Although rheology and chemistry of these systems are totally different from those of thermoplastics, it is interesting to note that extensional thinning was believed to be the main mechanism for cell opening in PU foam.

Based on the literature review, it is possible to produce low-density soft flexible absorbent open-cell thermoplastic foams. The most challenging step in the process is the stabilization of the newly created open cells within the foam. Once open, a cell can no longer retain the blowing agent and thus foam collapse cannot be avoided without a robust stabilization mechanism. The generation and stabilization of open cells is then

only possible through a good balance of elasticity and melt strength. Despite the limited amount of information available, some trends can be identified. In semi-crystalline resins (PE, EVA...), this balance of properties is mostly achieved through a partial cross-linking. Examples based on amorphous materials (styrenic homo-polymers and elastomers) suggest that the required balance of properties is more readily reached within this class of materials. The robustness of the foam stabilization mechanism found in amorphous systems is most likely explaining the ability to simultaneously generate low density and large open-cell content from such resins *without a chemical modification being required*.

3. Material Selection

Flexible materials can be classified into two distinct groups: soft copolymers made with soft and rigid segments and blends made with soft and rigid polymers. The rigid segments in flexible copolymers are usually generating a crystalline micro-phase alternating with blocks of soft, amorphous, segments. Examples of these are thermoplastic polyurethanes (*Elastollan, Texin, Pellethane*, etc), polyester-block-amides (*PEBAX*), block copolyesters (*Hytrel, Riteflex, Arnitel*, etc.), and random copolymers of ethylene and olefinic, acrylic, methacrylic, or vinyl monomers such as ethylene-octene, EVA, EMA, EBA, EEA, etc. Notable exceptions are the segmented SBS, SIS, SEBS, and SEP styrenic copolymers (*Kraton, Laprene, Calprene, Evoprene*, etc.) where both rigid and soft segments are amorphous materials. Soft polymer blends are also designed according to this concept. A crystallisable polymer (generally PP) is blended with a low glass transition temperature polymer (usually EPR or EPDM) to make a thermoplastic elastomer (*Santoprene, NexPrene, Sarlink*). The low T_g elastomer can be cross-linked to improve the overall TPE performance (called TPV) or left unmodified to minimize material cost (known as TPO). In addition to these two large classes of materials, there is a limited set of soft (or softenable) resins, including plasticized PVC and polycaprolactone. Note that PCL is one of the few biodegradable polymers commercially available on large scale.

To select proper materials for generating soft and flexible open-cell thermoplastic foams, materials must be screened for adequate mechanical properties. Low tensile modulus (or Young's modulus or modulus of elasticity) describes flexible materials that can generate soft and conformable foams. Another common industrial index is the Shore A and D Durometer Hardness Scales shown in Figure 1. Shore hardness is a measure of the resistance of a material to the penetration of a needle under a defined spring force. It is denoted as a number ranging between 0 and 100 on the A and D scales, the higher the number, the higher the hardness. Flexible materials are rated on the Shore A scale and rigid materials are rated on the Shore D scale. However, both scales partially overlap. Hardness and modulus are directly related, as shown in Figure 2. From this figure, Shore A hardness appears as a misleading measurement, especially in the high Shore A end where small value variations are translated in large modulus differences. However, the Shore A hardness is a convenient value reported by TPE producers while flexural moduli values are often more difficult to find. It must be kept in mind that foaming severely decreases a material modulus. As a first estimate, the relationship between foam modulus and density is typically a power-law behaviour with an index of 2 (that is, a ten-fold decrease in density induces a 100-fold decrease in modulus). Note that foam modulus is also related to its open-cell content. Dependence of foam modulus to open-cell content can be evaluated using Gibson and Ashby's Model [28]. Moduli calculated using their Model show fully open cell low-density foam is about 10 times

Hardness Comparison
Elastollan TPU & Other Materials

Figure 1: Hardness comparison of *Elastollan* thermoplastic PU (BASF) with other materials. The line at 60 Shore D is separating flexible PVC from rigid PVC. Figure reproduced from: *Elastollan Mechanical Properties Information Bulletin*, BASF.

Figure 2: Relationship between reported Shore A hardness and flexural modulus for some selected soft thermoplastic materials (data taken from supplier's datasheets).

more flexible than a 100% closed-cell foam of equivalent density. Although sensitivity of foam mechanical performance to open-cell content is much less important than its dependence to density, it is still significant.

The modulus criterion specified in Table 1 is rather subjective (flexible – cloth-like). Nevertheless, materials suitable for the type of foam sought for personal care wear should be soft enough to be described by the low-end of the Shore A hardness scale. For example, very low density LDPE foams (30 kg/m^3) are not flexible enough despite a base material hardness of 97-100 Shore A (flex modulus of 200-250 MPa) and a density reduction of more than 30-fold (*ca.* 10^3 modulus reduction based on unfoamed LDPE). As a first estimate, polymers and blends of polymers selected from the softest grades of materials described above should be suitable for fabricating low-density flexible open-cell foams. *Materials with Shore A hardness below 40-50 should be selected first (flexural modulus lower than 2-5 MPa)*. Preliminary experiments made at IMI tend to confirm this assessment. Medium-density closed-cell foams made from SIS terpolymer (located at 32 on the Shore A scale) produced cloth-like sheets while similar foams based on a harder SBS system (69 on Shore A) were significantly less flexible.

As listed in Table 1, compression resistance and set are also very important for personal hygiene products. Elastic materials can only be used, without permanent deformation, in the elastic zone. Only in this zone will materials recover to their original shape after stress has been removed. For *Elastollan* grades of thermoplastic polyurethane, a tensile strain of up to 10% deformation is possible for the more flexible grades (below Shore 95A). More rigid grades will support lower deformations. Therefore for any polymer type, selection for making resilient flexible foams should be made on the basis of a low hardness material; therefore, lower-the-hardness, the lower the compression set (%). This is also supporting the selection of very soft materials/grades as base resins for the project.

It must be kept in mind that thermoplastic elastomers are generally sophisticated materials and are often produced using proprietary technology. As a consequence, these materials are usually expensive. It is common to find thermoplastic elastomers sold at prices comparable to costs required for high performance engineering resins. This is especially true for block copolymers based on polyester, polyamide, and polyurethane chemistry, as well as the thermoplastic vulcanizates. Most of these materials will therefore not comply with the cost requirement stated in Table 1; i.e., 2.50$/lb. With the cost specification constraint, remaining polymers to evaluate are:

(1) Ethylene-based polymers such as LDPE, LLDPE, EVA, EEA, EMA, ethylene-octene, etc, and

(2) Styrenic-based elastomers such as SIS, SBS, SEBS, SEP, SEPS, etc., and

(3) Flexible PVC.

4. Recommendations

1-Low hardness materials

Aforementioned, the materials required to generate flexible and conformable foams should have a low hardness value (Shore A). Based on the information we obtained, we suggest that materials should have a hardness of 50 or less on the Shore A scale. This will enable sufficient flexibility and resiliency for the applications sought by Kimberly-Clark.

Required mechanical properties may be obtained either from single polymers or blends of polymers. In fact, most of the inexpensive commodity thermoplastic polymers such as LDPE and EVA have hardness values slightly higher than 95 Shore A. However, some LLDPE(s) and high VA content EVA(s) display Shore A values in the range selected. Many styrenic-based thermoplastic elastomers also comply to this hardness requirement. To adjust properties and maintain a reasonable production cost, it would be beneficial to use blends of polymers comprising a major fraction of commodity polymer(s); i.e., LDPE or EVA (commonly used in flexible shoe soles and mats manufacturing [6]), with a small amount of a low-hardness material compatible with the inexpensive matrix material. Blending polymers may also be beneficial to enhance open-cell formation as claimed by Bland *et al* [9]. In addition, amorphous systems are generally easier to foam than semi-crystalline polymers therefore focus should be put on these former systems (e.g. styrenic-based copolymers). Material properties can easily be tuned by adding PS homopolymer(s) and oil extenders, if needed.

At this stage, the best base resins for manufacturing the targeted foam appear to be, by order of preference:

a) Styrenic-based thermoplastic elastomers: SIS and SBS probably provide the best balance between properties and cost for this group of materials. The increased thermal/UV resistance of SEBS and SEP copolymers is probably not worth the extra cost, considering the targets product applications. Many grades offered are actually in the targeted Shore A hardness range. However, only a few are neat styrenic elastomers that have no oil extenders. Therefore, for minimizing potential extra complications from additives, the first experiments should focus on using such neat materials

b) Ethylene-based elastomeric copolymers: EVA and LLDPE, such as ethylene-octene copolymers with an EVA having 40% VA, and some high octene content EO copolymers show Shore A hardness in the selected range. These materials are usually inexpensive, especially EVA (42-49 ¢/lb). Extrusion of EVA may yield a slight vinegar-like smell but, according to its MSDS, no hazard issues are reported below its decomposition temperature (230°C).The low cost associated with such materials might not be totally true for EO elastomeric copolymers. Dow-DuPont is the sole supplier of these resins. Two distinct factors make ethylene elastomeric copolymers a second choice for the application: 1) the added complexity brought by the partial crosslinking required to adequately foam these resins, and 2) the expected narrower processing window (see Point #4, discussed below).

2- Use polymer grades that are either medical or FDA approved for direct skin contact

Since the applications sought by Kimberly-Clark require contact with the human body for extended periods of time, it is recommended that materials be chosen that are either medical grade or accepted for direct food contact by the FDA. This should limit the possible migration of minor species that are contained in the material (additives, oligomers, etc.).

3- Avoid flexible PVC (plasticizers)

PVC can be widely formulated into materials having various hardness. Moreover, it is inexpensive, which makes it interesting for making low-cost disposable devices. Unfortunately, flexible PVC contains a large content of low-molecular weight plasticizers (phthalates, etc.). This is especially true for the lower hardness PVC(s) specified here. These molecules are known to easily migrate out of the polymer matrix. The chemicals themselves can cause problems (allergies, toxicity, etc.) for wear applications requiring direct human contact. Moreover, as plasticizers migrate out of the polymer matrix, mechanical properties (i.e. flexibility) change. Therefore, there might be problems associated with the variation of these properties through time, shipment and storage of the products. Also in some areas of the world (Europe, for instance), there is strong pressure against the use of PVC. Such pressures might limit commercialization of a disposable personal care foam absorbent in these markets.

4- Generate open cells by controlling the extrusion temperature

NRC has been working with thermoplastic foams for many years and experience has shown that open cells can be formed by properly adjusting extrusion temperatures. An example for PS foam extrusion is illustrated below. The same phenomenon has also been reported in both patent and open literatures.
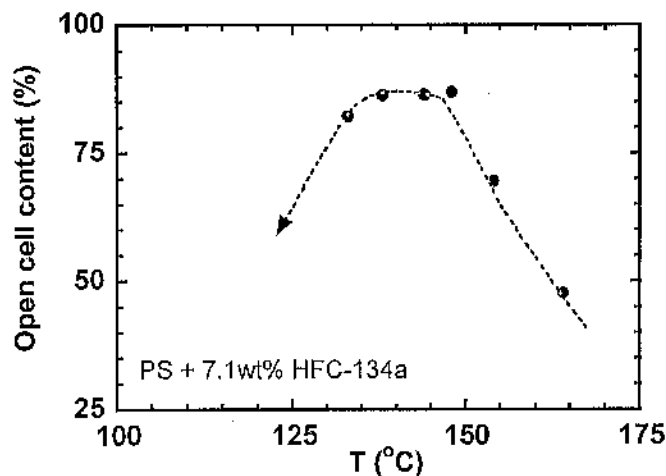

Figure 3. Variation of the open-cell content with temperature, for extruded PS foam combined with HFC-134a.

The melt temperature has to be adjusted so that bubble walls can rupture while maintaining the integrity of the foam structure. The proposed mechanism for the effect of temperature on cell rupturing is the following [29]. High nucleation density combined with large expansion yield thinner walls. Adequate melt strength provides foams integrity, while still enabling thin wall rupturing. This is schematically represented in Figure 4. Processing conditions will have to be optimized for a given foam polymer system, since these optimal processing temperatures are going to be different for every type of foam material selected (polymer and foaming agent). This is mainly due to the role that rheology plays during foam growth and cell rupture. Expansion is controlled by the viscous component (flow) while stabilization and rupture are mainly governed by the elastic part of the rheological response. The magnitude of this elastic component is function of the structure of the polymer (linear or branched), the temperature (and temperature sensitivity), and the rate of deformation (that is function of the foaming agent chosen, i.e. rate of diffusion).
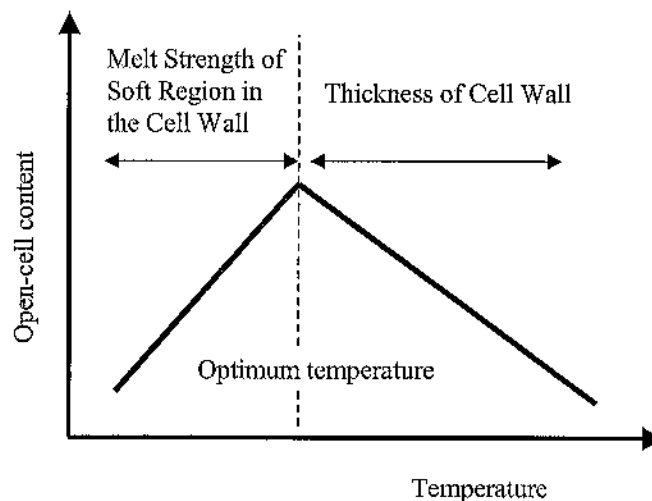
Figure 4. Two governing mechanisms for cell opening. (Excerpted from Ref.[29]).

In semi-crystalline systems, the processing window that allows the production of acceptable foam is narrow since lowering of the melt temperature is rapidly limited by crystallization. It is expected that the optimal processing window suitable to produce open-cell foams is within 5°C. Amorphous polymer systems rely on a different stabilization process. In this case, stabilization occurs when the viscosity of the polymer matrix rapidly increases with gas depletion. The viscosity of the matrix will play an important role in achieving open cells [23]. In addition, as there is no crystallization involved, the processing window leading to open-cell foams is much wider. Amorphous polymer systems are then largely preferred over semi-crystalline materials.

5- Generate open cells through rapid gas expansion

Rodeheaver and Colton [23] proposed that cell wall rupture is mainly controlled by the matrix's viscosity. They assumed that shear rates generated within the films are small and that the non-Newtonian behaviour of these films can be simply ignored. Nonetheless, NRC observed that gas diffusing more slowly out of the bubble will less likely produce open cells. This would indicate that the capability of a bubble to sustain

deformation is not only a function of the maximum stress applied but also a function of the deformation rate (i.e. shear rate). This is explained since the polymer structure has enough time to stabilize within the time frame of the bubble expansion. In turn, typical fast diffusing gas species such as carbon dioxide, nitrogen or HFC-134a, will rupture cell walls unless the process is sufficiently controlled. This feature can be advantageously used for the purposes sought by Kimberly-Clark. More specifically, use of inert gases (such as CO_2 or N_2 or a combination of gases) will also enable the production of foam at the lowest cost, compared to hydrocarbons, HCFC(s) or HFC(s), while eliminating potential toxicological/environmental/safety hazards. Should inert gases prove inadequate to reach low densities, as required by Kimberly-Clark, a combination of inert gas(es) and a minor phase of a low-volatility agent, such as low molecular weight alcohols, may be used to produce low-density foams.

<u>6- Adding immiscible components to increase open-cell content</u>

Multiple patents claim the use of immiscible components as cell opening additives in foams. The diversity of systems covered in these various patents (see Tables B1 and B2) leads one to consider polymer blending as a generic technique for increasing open-cell content. In cases where open-cell content obtained by controlling the extrusion conditions would not be adequate, adding immiscible components to the base elastomeric system would be a way to further open foam cells. However, experience showed that blending polymers should be done with great care. Immiscible polymer blends are notorious for their poor mechanical properties. Immiscible component selection should be made carefully to ensure that some level of interaction (*compatibility*) exists between the blend's components. There is a large amount of formulation, process and equipment literature available on this topic and its review exceeds the scope of this report.

<u>7- Adding nucleating agents to generate open cells</u>

Nucleating agents are generally used to control the cell size distribution in foam. However, these solid particles also disrupt, to some extent, the polymer matrix. Champagne [30] studied the impact of nucleating agents on the formation of low-density LDPE foams (density, cell size, and open-cell content) and showed that the nature of the particle greatly affects the extensibility of the polymer matrix. Loss of extensibility caused by the particles is likely responsible for generating a higher fraction of open cells. Reported results showed that talc and polytetrafluoroethylene powder (PTFE) produced higher open-cell content than calcium carbonate or calcium stearate in LDPE foams. This particular feature of nucleating agents can be exploited to customize the level of open porosity for producing absorbing devices.

5. *Proposed NRC Work Plan*

Different strategies can be used to produce open-cell foam as described in the Recommendations Section. Each of them can be used separately or in combination with each other to produce the desired foam quality (foam density, cell-size distribution, and open-cell content). The number of systems that can be tested are numerous considering that each flexible material chosen can be tested under a variety of temperature conditions, blowing agent levels, and type of additives employed to form open cells while

maintaining a low density. However, some resins, blowing agents, and methods seem, at this stage, potentially more successful in generating the type of foam targeted by Kimberly-Clark.

The approach proposed is based of a two-step process. The first step is a series of experiments to screen different polymer formulations, blowing agents, and processing setups for reaching approximate flexibility, open-cell content, and density requirements. The second step will focus on optimizing the best formula as identified in Step 1.

Step 1: Material Selection and Foam Extrusion

The objective of this first phase of the project would be as follow:

1) To select the best material for generating high open-cell content and low density,
2) To identify the most suitable grades for reaching the targeted flexibility requirements,
3) To gather data on systems' rheologies and solubilities for optimizing process design,
4) To choose the proper blowing agent type (or blowing agent blend) and content for generating the desired cell density, morphology, and structure, and
5) To estimate the approximate width of the processing window to produce extrusion foams with the targeted properties.

The proposed project would be conducted iteratively, starting with short extrusion experiment sequences and alternating with basic foam characterization to enable the early elimination of unsuitable materials/grades. Materials/formulations will be selected based on flexural modulus and viscosity data to indicate a substantial chance for foaming to a low density.

Low-density foaming is generally performed with resins that exhibit low shear viscosity (suitable grade for extrusion) but high enough melt strength. For semi-crystalline resins, preferred polymer chain structure is long chain branchings, that induces very long relaxation times and strain hardening feature, i.e. increase of the viscosity with magnitude of the deformation. For styrenic-based resins, this "melt strength" requirement is less stringent, since the polymer undergoes large viscosity increase (including elasticity) during expansion as the foaming agent phase separates from the polymer matrix. Rheology of polymer blends is rather complex, and can benefit from synergy of the two (or more) components. It is a common practice to have one component selected for its benefit on the processability (like a high-melt-strength resin to ease the foaming process), while the second polymer aims at providing specific physical or mechanical properties for the end product. However, extrapolation of blend's behavior from its components' properties is not straightforward, and this issue should be addressed correctly when designing the characterization and experimental plans.

Materials/formulations not leading to low density flexible foam would be readily eliminated after a few rounds of experiments. By this extrusion-foaming approach, screening of a large number of potentially useful materials/grades would be accessed. The most promising materials/formulations/grades (one or two, maximum) would then be extensively evaluated for assessing the influence of processing conditions on foam density, open-cell content, and structure.

Results will be summarized in a report and delivered to Kimberly-Clark. NRC and Kimberly-Clark will both evaluate the results and select one system for Step 2. At this point, collaborators may choose to stop the project if results should not prove sufficiently promising.

Step 2: Process Optimization and Foam Functionalization

The second step of the development process will be dedicated to optimizing the formulation to meet the requirements to produce acceptable absorbent foam. Additives and selected modifications to processing conditions may be required to maximize open cells (i.e. absorbency), maintain low density, and adjust the cell size; e.g., for optimizing wicking rate. Since all potential materials identified so far for this project are mostly hydrophobic, other additives (surfactants etc.) will be needed to improve wettability. Formulations will be characterized at IMI for density, open-cell content, complete morphology, and mechanical behavior. KCC will complete the characterization tasks by providing information relative to foam absorbency performance. Objectives of this phase of the project are:

1) To optimize the system developed in Step 1 in terms of foam characteristics and extrusion conditions,
2) Formulate the foam identified in Step 1 to produce an acceptable absorbent foam complying with all the requirements stated in Table 1, and
3) Gather data on the foam system's rheology and solubility for optimizing the final formulation/process design.

Step 2 will be a classical straightforward method where all conditions will be defined conjointly with KCC representatives and experiments will be ran in one or two sequences. The results will be used to establish relationships between compositions, extrusion conditions, and foam properties. Once completed, the project's final results will be compiled in a report for Kimberly-Clark.

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ANNEX A: Details of the Search Strategies

The research was conducted by using the combinations of concepts described below. Exact phrasing of keywords and logical operators used are also reproduced for reference purpose.

A- Flexible or soft material

soft or flexible or conformable or elastomeric or elastomer(w)based or rubbery or rubber(w)like

B- Thermoplastic polymers, including thermoplastic polyurethanes but excluding thermoset polyurethanes using chemical abstract classifications (CAS number)

(TPU or urethane#(w)polymer# or polyurethane# or poly(w)urethane# or Urethane(w)rubber# or ((urethane# or polyurethane# or pu or pur)(2a)elastomer?) or (thermoplastic(2w)(elastomer# or rubber#))) and l2
Ly s tsur or (thermoset?(s)(polyurethane# or poly(w)urethane# or pu or pur or urethane#))

C- Thermoplastic materials, including thermoplastic elastomers and rubbers

(thermoplastic# or thermo(w)plastic# or tpu or tpur or tpe# or tpr or tpo)

D- Polymeric foams

(((plastic# or polymer# or thermoplastic# or thermo(w)plastic# or resin#)(s)(foam# or cellular or micro(w)cellular or microcellular)) or extru?(a)foam# or ((urethane or polyurethane or poly(w)urethane or thermoplastic)(2a)(rubber# or elastomer?)))

E- Open cell foams or porous materials

open? (w) (cell# or porosity?)

F- Low density (optional)

low?(w)densit ? or expansion

Combination of the selected different concepts created the three reference sub-sets, as reported in Table A1. A brief description of the 28 titles found during this literature search is given in Table A2.

Table A1. Research Strategy Used for the Literature Search

Combinations	Number of titles	Titles selected	Full selected reference
Concept A & Concept B & Concept C & (Concept D (s) Concept E) & Concept F	1	1	1
(Concept A & Concept B & Concept C & (Concept D (s) Concept E)) excluding previous titles	5	0	0
(Concept A & (Concept B or Concept C) & (Concept D (s) Concept E)) excluding previous titles	28	11	11

Table B1. Selected Titles for the Literature Search

Relevance	Full Title	Full Reference	Comment
High	Moisture Vapor-Transmitting Adhesive Wound Dressings	Source: US 4753231 U.S., 6 pp. Cont. of U.S. Ser. No. 794,753, abandoned. CODEN: USXXAM Inventors: Lang, Stephen M.; Webster, David F. Patent Assignee: Smith and Nephew Associated Co. PLC, UK Document Type: Patent	Useful information provided in text.
High	Adhesive Wound Dressing	Source EP 99748 Inventors: Lang, Stephen Michael; Webster, David Fitzgerald Eur. Pat. Appl., 30 pp. CODEN: EPXXDW Document Type : Patent	Cross-reference with previous patent
High	Ethylene Polymer Foam Compositions	Source US 3544490 U.S., 4 pp. CODEN: USXXAM Inventors : Alexander, Richard L.; Ashburn, Donald G.; Clampitt, Bert H.; Anspon, Harry D. Document Type : Patent	Useful information provided in text.

High	Wound Dressing And Its Use	Source EP 106439 Inventors: Lang, Stephen Michael; Webster, David Fitzgerald Eur. Pat. Appl., 22 pp. CODEN: EPXXDW Document Type: Patent	Cross-reference with previous patent
High	Poromers Based On Thermoplastic Elastomer Block Copolymers.	Authors: Ghioca P; Buzdugan E; Cerchez I; Stancu R; Banica G (ICECHIM) Source: Materiale Plastice 27,No.4,Oct/Dec.1990,p.176-80 Document Type : journal article	Language: Romanian Reference not obtained
Moderate	Custom-Formable Shoe Insert	Source WO 2000025616 PCT Int. Appl., 30 pp. CODEN: PIXXD2 Inventors: Ersfeld, Dean A.; Anderson, Richard E.; Ruegsegger, Michael L.; McGurran, Kelly T.; Mallo, Richard A. Patent Assignee: 3M Innovative Properties Company, USA Document Type: Patent	May provide useful information for making flexible foams
Moderate	Durability Testing Of An Elastomeric Foam For Use In Hydraulic Accumulators	Source: Proceedings of the Intersociety Energy Conversion Engineering Conference (1988), 23rd(Vol. 2), 31-6 Author: Pourmovahed, A. Document Type: journal article	May contain useful information on open cell PU rubber foams.
Moderate	Open-Celled Foams	Source DE 2728573 Ger. Offen., 26 pp. CODEN: GWXXBX Inventors :Shikinami, Yasuo; Kusatsu, Shiga; Iida, Kosuke; Hata, Kunihiro; Kasajima, Fumio Patent Assignee: Takiron Co., Ltd., Japan Document Type : Patent	Language: German Reference not obtained Elastomeric foam made with cross-linker and chemical blowing agent
Moderate	Pore-Filled, Open-Celled Plastic Foam	Source GB 1127057 US 3471419 Brit., 5 pp. CODEN: BRXXAA Inventor : Ehrlich, Joseph R. Document Type : Patent	May contain useful information on resilient foams.

Moderate	Gelatinous Elastomer Articles	Source US 5336708 A 19940809 Inventor : Chen J Y Patent Assignee Applied Elastomerics Inc. CA Pacifica, Calif., USA Document Type : Patent	
Moderate	Porous Cellular Urethane Provides Support, Spring Force In Elastomeric Connectors	Source: Urethane Plastics and Products 14,No.2,Feb.1984,p.2-4 ISN: 0049-5700	May contain useful information
Moderate	Shoe Bottom	Source :GB 2016259 Inventor: KRUG H D; MILDENBERGER W Patent Assignee: CARL FREUDEN BERG. Document Type: Patent	May contain useful information
Low	Two Years Of Industrial Experience With Liquid Carbon Dioxide Blown Slabstock Foams.	Reference not obtained	
Low	Use Of Blowing Catalysts For Integral Skin Polyurethane Applications In A Controlled Molecular Architecture Environment: Synthesis And Impact Of Ultimate Physical Properties.	Reference not obtained	
Low	AEI Cables. Company Profile	Reference not obtained	
Low	Non-Reactive Surfactants Improve Polyurethane Processing	Reference not obtained	
Low	Creep/Recovery Behavior Of Open-Cell Foams	Reference not obtained	
Low	Compressional Behavior Of Inked Open-Cell Foams	Reference not obtained	
Low	Cellular Carbon Structure And Method For Producing Same	Reference not obtained	

Low	The Development Of A Sound Insulation Package For Car Floor Coverings Using A Combination Of Polyurethane Technologies	Reference not obtained	
Low	Imitation-Leather Material	Reference not obtained	
Low	R/BAK Improves Flexo Print Quality	Reference not obtained	
Low	Microbuckling Instability In Elastomeric Cellular Solids	Reference not obtained	
Low	Peristaltic Pump For High-Solids Slurries	Reference not obtained	
Low	Laminated Bandage	Reference not obtained	
Low	Government-Owned Inventions; Availability For Licensing	Reference not obtained	
Low	Properties Of Rigid Polyurethane Foam Under Hydrostatic Pressures	Reference not obtained	
Low	Reinforced Plastic Parts From Low-Pressure Moulds	Reference not obtained	
Low	Contribution Of Elastomeric Insulated Cables To The Solution Of Energy Problems	Reference not obtained	
Low	Use Of Blowing Catalysts For Integral Skin Polyurethane Applications In A Controlled Molecular Architectural Environment: Synthesis And Impact On Ultimate Physical Properties	Reference not obtained	
Low	Cellular Plastics	Reference not obtained	
Low	Mechanical Behavior Of Microcellular Foams	Reference not obtained	

Table B2: Brief Description of Selected US Patents Relevant to Open-Cell Foam Manufacturing (patents are presented by order of relevance to the project.).

No Patent	Year	Assignee	Title	Composition	Product	Examples / Comments
6,541,533	2003	JSP Corporation	Extruded polyolefin resin foam	Blend with : A. Ethylene ionomer resin (10-45 wt%), B. polyolefin resin (PP, LLDPE, HDPE, melting point greater than 120°C, 1-15 wt%, for shape retention), C. Other (EPR, styrene elastomers, PE resin, melting point lower than 120°C, 40-70 wt%, low melt tension component), D. Anti-shrinking agent (fatty acid, GMS,...), nucleating agent, either physical or chemical foaming agent	Open cell content greater than 50%, foam density 15-200 kg/m^3	Closed-cell foam with less than 4.5wt% of ethylene ionomer resin (A); Component B less than 0.5wt%: No shape retention; Component C more than 95wt%: closed-cell foam. Soft to the touch with open cell ratio greater than 70%.
5,962,545	1999	Dow Chemical	Method of enhancing open cell formation in alkenyl aromatic polymer foams	Alkenyl aromatic polymer (with more than 50wt% of alkenyl aromatic monomeric units, PS), nucleating agent, blowing agent (HFC, HCFC, CO$_2$. Enhancement through incorporation of ethylene copolymer (0.1-7wt%; ethylene monomeric content of 50-90wt%; EVA, EAA, ionomer, EMAA, EMA, EEA) having a Vicat softening point of 85°C or less	Open cell content of 30% or more; foam density of 16-250kg/m^3, cell sizes of 1.2mm or less.	PS/EVA (3wt%)+ HFC-134a (8.8phr)+ethyl chloride (2.5phr)+CO$_2$ (1.1phr) : ρ=39.2-45.5 kg/m^3; OCC= 54.1% (113°C) 95.2% (119°C)
6,071,580	2000	Dow Chemical	Absorbent, extruded thermoplastic foams	Alkenyl aromatic polymer (PS, with more than 50wt% of alkenyl aromatic monomeric units), nucleating agent, physical blowing agent; non-crosslinked foam.	Open cell content of 50% or more (up to 95%), with cell sizes from 5 μm up to 1.5mm; absorbency can be enhanced by applying a surfactant; foam density 16-250 kg/m^3.	Extrudate is elongated as it exits and expands. Diaper is mentioned as application.

No Patent	Year	Assignee	Title	Composition	Product	Examples / Comments
6,093,752 6,174,471	2000 2001	Dow Chemical	Open-cell foam and method of making	Blend of PS and ethylene-styrene interpolymer; physical foaming agent (carbon dioxide); nucleating agent	Open cell content greater than 80%	ESI resin no longer available
4,931,484 5,059,631 5,098,782 5,277,515 5,387,050	1990 1991 1992 1994 1995	Applied Extrusion Technologies Nomaco	Extruded ethylenic polymer foam containing both open and closed cells	Ethylenic polymer (LDPE, EVA or blend of LDPE (85-10%)/EVA (15-90%)),	Low-density (1.5-10 lb/ft^3) ethylenic polymer foam containing 30-85% open cells with integral surface.	Superior compression recovery;superior moisture resistance; non-out gassing.
5,780,521	1998	Dow Chemical	Extruded, open-cell microcellular alkenyl aromatic polymer foams, process for making, and articles made therefrom	Alkenyl aromatic polymer (PS, with more than 50wt% of alkenyl aromatic monomeric units), physical foaming agent (HCFC, HFC, CO2), nucleating agent	Open cell content of 70% or more, cell sizes of 70µm or less, density 25-100 kg/m3	"The use of a relatively small amount of blowing agent allows formation of a foam with a high open cell content." Also relies on high processing temperature.
5,411,687 5,434,195 5,674,916 5,693,687 5,824,710	1995 1995 1997 1997 1998	Dow Chemical	Extruded, open-cell alkenyl aromatic polymer foam and process for making	Alkenyl aromatic polymer (PS, with more than 50wt% of alkenyl aromatic monomeric units), nucleating agent, blowing agent (carbon dioxide, HFC, ethyl chloride)	Open-cell (30-80%) alkenyl aromatic polymer foam, high heat distortion temperature (175-210ºF),foam density: 1.5-6.0 pcf/16-100 kg/m^3, cell sizes: 0.08-1.2mm.	Mostly rely on elevated foaming temperatures; interest driven by Vacuum Insulation panels (VIP) technology
5,348,795	1994	Dow Chemical	Process for making a dimensionally-stable open-cell polypropylene foam with organic blowing agents	Propylene polymer material (PP, preferably HMS-PP, or copolymers of propylene), with greater than 50wt% of propylene monomeric units; PFA (aliphatic hydrocarbons, HFC, HCFC, CFC, aliphatic alcohols).	Low-density (less than 96 kg/m^3) polypropylene foam, with greater than 20% open cells (typically 30-70%, function of processing temperature); cell sizes of 2mm or less.	

No Patent	Year	Assignee	Title	Composition	Product	Examples / Comments
6,666,998	2003	Reifenhauser GmbH Co.	Method and device for producing at least partially open-cells foam films from styrene polymers	PS (100 pts), immiscible polymer (PO, EVA,1-3pts), surfactant (0.5-3.5 pts), nucleating agent (0.5-3pts), physical foaming agent (2-6wt%)	Foam density 40-100 kg/m^3, open cell content of at least 25%	
4,142,956	1979	Takiron	Process for producing an open cell foam	Thermoplastic resin polymer blend including 1,2-polybutadiene (10-90wt%) and one from polyolefin (PE, PP, PB), vinyl copolymer (EVA, EVOH, EA, EP, PB copolymers) or butadiene copolymer (ABS, SBR); photosensitizing agent; chemical foaming agent.	Open cell (50-98%) foam; expansion ratio: 20 or more.	Irradiation with ultraviolet light
4,384,032	1983	Asahi-Dow Ltd	Fluid transmitting polyolefin foams and method of making the same	Blend of polyolefin (PE, PP) and styrene or methacrylic acid ester polymer (1-99wt% from PS, PMMA or ABS); chemical or volatile blowing agent.	Foam with density less than 0.5 g/cm^3 (expansion in the range of 1.2-5.0) cell size less than 0.1 mm; strong, elastic, soft.	
6,251,319	2001	Dow Chemical	Method of forming a thermo-formable polypropylene sheet	Polypropylene, physical foaming agent	PP foam with density 16-200 kg/m^3, open cell content less than 70%, cell sizes of 0.1-6.0 mm.	
3,950,278	1976	Sumitomo Chemical Company	Process for producing a crosslinked foam of polyolefin resin having open cells	Crosslinkable polyolefin resin (LDPE, HDPE, EVA), 20-60wt% of amorphous propylene polymer, chemical foaming agent, crosslinking agent (peroxide)	Crosslinked foam having uniform, fine, open cells (40% or more) foaming ratio: 7-8	
4,877,814	1989	Kabushiki Kaisha Serutekuno	Process for producing open-cell polyethylene foam material and the resultant product	Polyethylene or ethylene copolymer; chemical foaming agent and crosslinking agent.	Expansion ratio of 25 times; open-cell ratio from 96-100%.	Mechanical compression to rupture cell membranes.

No Patent	Year	Assignee	Title	Composition	Product	Examples / Comments
4,381,962	1983	Lonseal Corporation	Method for producing an open cell foam from a polyvinyl chloride resin produced by suspension polymerization	Polyvinyl chloride resin (emulsion polymerization), organic stabilizers, a surface active agent and chemical foaming agent	Open cell foam of flexible PVC resin: foam leather characterized through breathability and water permeability.	
4,425,442	1984		Process for producing open cell foam and foamable compound			
4,797,426	1989		Hard polyvinyl chloride resin composition and open-cell foam made of said composition			
4,424,181	1984	Nippon Unicar Company	Process and composition for producing open-cell crosslinked polyolefin foam	Olefin resin (100 parts by wt), chemical blowing agent (20pts), crosslinking agent (peroxide, 0.3-10 pts), trifunctional monomer (0.1-10pts) and silicone oil (1-5 pts).	Open-cell crosslinked polyolefin foam; breathability, water absorption, weather resistance, flexibility; foam density: 115-165 kg/m^3, cell sizes: 0.2-0.6 mm.	
4,499,210	1985	Union Carbide Corp.				
5,100,924	1992	Nippon Unicar Company	Open cell foam composition	PE or ethylene copolymer (EVA, EEA); organopolysiloxane (at least 250 units of siloxane) such as silicone gum or silicone oil; chemical blowing agent (optionally: a monomeric diene with 5-20 carbon atoms; organic peroxide, for a gel content of at least 10wt%)	Open cell foam, cell diameter: 0.1-0.3 mm	
4,581,383	1986	Dow Chemical	Lightly crosslinked linear olefinic polymer foam blends and process for making	Blend of linear olefin polymer (such as LLDPE, 5-95wt%) and crosslinkable polymer (95-5 wt%) with functional groups; crosslinking agent and volatile blowing agent (CFC).	Foam density: 30-290 kg/m^3, cell size: 1-2 mm; open cell content: 60-90%.	