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(54) **Title:** PROPYLENE BASED MELTBLOWN NONWOVEN LAYERS AND COMPOSITE STRUCTURES

(57) **Abstract:** The present invention relates to propylene-based nonwoven layers made by the meltblown process, and laminates incorporating such layers. The meltblown layers of the present invention comprise propylene copolymers characterized by having less than 50 percent crystallinity. The meltblown layers of the present invention show an improved combination of extensibility and tensile strength. The laminate structures of the present invention are characterized by a combination of low bending modulus with high peel strength.



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PROPYLENE BASED MELTBLOWN NONWOVEN LAYERS AND  
COMPOSITE STRUCTURES

Field of the Invention

The present invention relates to propylene-based nonwoven layers made by the  
5 meltblown process, and laminates incorporating such layers. The meltblown layers of the  
present invention comprise propylene copolymers characterized by having less than 50  
percent crystallinity. The meltblown layers of the present invention show an improved  
combination of extensibility and tensile strength and also exhibit markedly better bonding  
strength when bonded to spunbond layers, particularly spunbond layers made from fibers in  
10 which a polyethylene based material comprises at least a portion of the surface.

Background and Brief Summary of the Invention

Nonwoven webs or fabrics are desirable for use in a variety of products such as  
bandaging materials, garments, disposable diapers, and other personal hygiene products,  
including pre-moistened wipes. Nonwoven webs having high levels of strength, softness,  
15 and abrasion resistance are desirable for disposable absorbent garments, such as diapers,  
incontinence briefs, training pants, feminine hygiene garments, and the like. For example,  
in a disposable diaper, it is highly desirable to have soft, strong, nonwoven components,  
such as topsheets or backsheets (also known as outer covers).

As used herein, the term "nonwoven web", refers to a web that has a structure of  
20 individual fibers or threads which are interlaid, but not in any regular, repeating manner.  
Nonwoven webs have been, in the past, formed by a variety of processes, such as, for  
example, air laying processes, meltblowing processes, spunbonding processes and carding  
processes, including bonded carded web processes. These various process each have their  
own strengths and weaknesses. For example, spunbonded webs tend to have higher tensile  
25 strength than meltblown webs whereas the meltblown process tends to produce webs having  
increased liquid barrier properties as compared to spunbond nonwovens.

Propylene-based polymers, particularly homo-polypropylene (hPP) are well known  
in the art, and have long been used in the manufacture of fibers. Fabrics made from hPP,  
particularly nonwoven fabrics, exhibit high modulus but poor elasticity and softness.  
30 Nevertheless, these fabrics are commonly incorporated into multicomponent articles, for  
example, diapers, wound dressings, feminine hygiene products and the like.

In comparison, polyethylene-based elastomers, and the fibers and fabrics made from these polymers, tend to exhibit low modulus and good elasticity, but they also tend to have low tenacity, stickiness and exhibit a hand feel which is generally considered as unacceptable for many applications.

5 Tensile strength of nonwovens and tenacity of fibers is important because the manufacture of multicomponent articles typically involves multiple steps (for example, rolling/unrolling, cutting, adhesion, etc.), and webs lacking tensile strength may not survive one or more of these steps. Fibers with a high tensile strength (also known as tenacity) are also advantaged over fibers with a low tensile strength because the former will experience  
10 fewer line breaks, and thus greater productivity will be obtained from the manufacturing line. Moreover, the end-use of many products also typically requires a level of tensile strength specific to the function of the component. Tensile strength must be balanced against the cost of the process used to achieve the higher tensile strength or to achieve higher tenacity. Optimized fabrics will have the minimum material consumption (basis  
15 weight) to achieve the minimum required tensile strength for the manufacture and end-use of the fiber, component (for example, nonwoven fabric) and article.

Hand feel is another important aspect for many nonwoven structures, particularly those structures intended for use in the hygiene and medical field. Low modulus is one aspect of hand feel. Fabrics made from fibers with a low modulus will feel "softer", all else  
20 being equal, than fabrics made from fibers with a high modulus. A fabric comprised of lower modulus fibers will also exhibit lower flexural rigidity which translates to better drapability and better fit. In contrast, a fabric made from a higher modulus fiber, for example, hPP, will feel harsher (stiffer) and will drape less well resulting in a poorer fit. Fabrics made from polyethylene-based elastomers also tend to lack adequate hand feel as  
25 they tend to have an undesirable feel to the skin commonly characterized by descriptors such as tacky, sticky, clammy, rubbery, or wet.

Fiber extensibility/elasticity is another important criteria for nonwoven structures, particularly those used in hygiene and medical applications, because the characteristic translates to a better comfort and fit as the article made from the fiber will be able to be  
30 more body conforming in all situations. Diapers with elastic components will have less sagging in general as body size and shape and movement vary. With improved fit, the

general well being of the user is improved through improved comfort, reduced leakage, and a closer resemblance of the article to cotton underwear.

A nonwoven meltblown layer which exhibits a combination of high tensile strength, good elongation and adequate hand feel is therefore desired and is an aspect of the present invention. It has been discovered that such extensible/elastic meltblown fabrics can be made from a particular class of polypropylene, known as propylene based plastomers and elastomers, without the need for blending substantial amounts of higher tenacity materials such as hPP. The propylene based plastomers and elastomers can be characterized by one or more of the following traits: crystallinity less than 50 percent; flex modulus less than 50 kpsi; melting point less than about 140° C (and even less than about 130<sup>0</sup>C); and/or heat of fusion less than 80 J/g. The propylene based polymer preferably comprises copolymers of propylene and an alpha-olefin, and the alpha olefin is preferably ethylene. The ethylene in the preferred embodiment is preferably present in an amount of from 3 to 20 percent by weight of the propylene based polymer. Propylene based polymers having ethylene in an amount of from 9 to 20 percent by weight of the propylene based polymer are more elastomeric. Such polymers may be referred to as propylene-based elastomers (PBE). The preferred propylene based polymer has an MWD of from 2 to 4. The propylene based polymer typically may have a melt flow rate (prior to any rheology modifier) in the range of from 1 to 100 g/10 min. Nonwoven meltblown layers made from propylene based plastomers and elastomers, without substantial amounts (such as more than about 10 percent by weight (10 wt.percent)) of hPP is therefore another aspect of the present invention. All percentages specified herein are weight percentages unless otherwise specified.

By themselves, for example, these nonwovens may advantageously be used in filtration applications, or they may be combined with other materials, including other nonwoven materials. For structures can have hydrohead performance from 100, preferably 200 to 800 mm H<sub>2</sub>O for a 25 gsm basis weight. Higher basis weights may be able to achieve higher hydrohead performance.

Used in combination with other materials such as another nonwoven, film, apertured film, fibers, woven fabric or others, synergistic properties may be achieved. It is recognized that performance requirements will vary with applications. As a result, use of this invention and its various embodiments can take a number of forms not limited to the descriptions provided herein.

Because of the relative strengths and weaknesses associated with the different processes and materials used to make nonwoven fabrics, composite structures of more than one layer are often used in order to achieve a better balance of properties. Such structures are often identified by letters designating the various layers such as SM for a two layer structure consisting of a spunbond layer and a meltblown layer, SMS for a three layer  
5 structure consisting of a spunbond layer and a meltblown layer, SMS for a three layer structure, or more generically  $SM_xS$  structures. In order to maintain structural integrity of such composite structures, the layers must be bonded together. Common methods of bonding include point bonding, adhesive lamination, and other methods known to those skilled in the art. It is a continual goal within the art to increase the bonding strength  
10 between the layers in order to provide more durable structures as long as other desirable properties such as breathability and flexural modulus are preserved to a certain degree.

It has been observed, however, that poor bonding strength between layers is particularly problematic when polyethylene materials (including bicomponent fibers where polyethylene forms at least part of the surface of the bicomponent fibers) are used to make one layer, and propylene materials such as homopolymer polypropylene ("hPP") or random  
15 copolymer polypropylene ("RCP") are used for an adjacent layer. It would therefore be particularly desirable to improve the bonding strength between polyethylene-based layers and polypropylene-based layers in a nonwoven composite structure.

It has also been discovered that meltblown fabrics made from this particular class of polypropylene based materials offers superior bonding strength to spunbond layers made from fibers having surfaces comprised of polyethylene based materials. In addition to providing superior bonding strength between the meltblown and spunbond layers, the use of these polymers for use in the meltblown nonwoven webs has been observed to increase the overall softness as compared to composites in which the meltblown layers comprise  
20 substantial amounts of hPP or RCP.

Another aspect of the present invention is a nonwoven laminate comprising a meltblown nonwoven layer and a spunbond nonwoven layer wherein the meltblown layer comprises meltblown fibers comprising a propylene based polymer characterized by having one or more of the following traits: less than 50 percent crystallinity; flex modulus less than  
30 50 kpsi; melting point less than about 140° C; and/or heat of fusion less than 80 J/g. The propylene based polymer preferably comprises copolymers of propylene and an alpha-olefin, and the alpha olefin is preferably ethylene. The ethylene in the preferred embodiment is

preferably present in an amount of from 3 to 20 percent by weight of the propylene based polymer. The preferred propylene based polymer has an MWD of from 2 to 4. The preferred propylene based polymer has a melt flow rate (prior to any rheology modifier) in the range of from 1 to 100 g/10 min.

5 In another aspect of the nonwoven laminates of the present invention, the spunbond layer comprises fibers characterized in that a polyethylene based material comprises at least a portion of the surface of the fiber, The spunbond layer in the nonwoven laminates of the present invention may comprise a bicomponent fiber, and if so the bicomponent fiber is preferably in a sheath-core configuration. Alternatively the spunbond layer may comprise a  
10 monofilament fiber (that is, the fiber will have a uniform cross section).

Another aspect of the present invention is a nonwoven laminate structure comprising at least two nonwoven layers, said nonwoven laminate structure being characterized by having an overall bending modulus less than 0.005 Nmm and a peel strength between the nonwoven layers of more than 2 N/5cm width.

15

#### Brief Description of the Drawings

Fig. 1 is a plot of Bending Modulus vs. Elongation for the examples and comparative examples indicated;

20 Fig. 2 is a plot of Peak Force vs. Elongation for the examples and comparative examples indicated;

Fig. 3 is a plot of Set Strain vs. Elongation for the examples and comparative examples indicated;

Fig. 4 is a plot of Retained Load vs. Elongation for the examples and comparative examples indicated;

25 Fig. 5 is a bar graph showing the bending modulus for laminate structures as indicated; and

Fig. 6 is a bar graph showing the peel strength for laminate structures as indicated.

#### Detailed Description of the Invention

30 As used herein, the term "nonwoven web" or "nonwoven fabric" or "nonwoven", refers to a web that has a structure of individual fibers or threads which are interlaid, but not in any regular, repeating manner. Nonwoven webs have been, in the past, formed by a

variety of processes, such as, for example, air laying processes, meltblowing processes, spunbonding processes and carding processes, including bonded carded web processes.

As used herein, the term "meltblown" , refers to the process of extruding a molten thermoplastic material through a plurality of fine, usually circular, die capillaries as molten threads or filaments into a high velocity gas (for example, air) stream which attenuates the filaments of molten thermoplastic material to reduce their diameter, which may be to a microfiber diameter. Thereafter, the meltblown fibers are carried by the high velocity gas stream and are deposited on a collecting surface to form a web of randomly dispersed meltblown fibers.

As used herein, the term "spunbonded", refers to the process of extruding a molten thermoplastic material as filaments from a plurality of fine, usually circular, capillaries of a spinneret with the diameter of the extruded filaments then being rapidly reduced by drawing the fibers and collecting the fibers on a substrate.

As used herein, the term "microfibers", refers to small diameter fibers having an average diameter not greater than about 100 microns. Fibers, and in particular, spunbond and meltblown fibers used in the present invention can be microfibers. More specifically, the spunbond fibers can advantageously be fibers having an average diameter of 15-30 microns, and having a denier from 1.5-3.0, whereas the meltblown fibers can advantageously be fibers having an average diameter of less than about 30 microns, or more advantageously be fibers having an average diameter of less than about 15 microns, or even more advantageously be fibers having an average diameter of less than about 12 microns. It also contemplated that the meltblown fibers may have even smaller average diameters, such as less than 10, 8 or even 5 microns.

As used herein, the term "polymer" generally includes, but is not limited to, homopolymers, copolymers, such as, for example, block, graft, random and alternating copolymers, terpolymers, etc., and blends and modifications thereof. Furthermore, unless otherwise specifically limited, the term "polymer" shall include all possible geometrical configurations of the material. These configurations include, but are not limited to, isotactic, syndiotactic and random symmetries.

As used herein, the term "polypropylene based plastomers (PBP) or elastomers (PBE)" (collectively, these may be referred to as "PBPE") includes reactor grade copolymers of propylene having heat of fusion less than about 100 Joules/gm and MWD <

3.5. The PBPs generally have a heat of fusion less than about 100 Joules/gram while the PBEs generally have a heat of fusion less than about 40 Joules/gram. The PBPs typically have a weight percent ethylene in the range of 3 to 10 wt percent ethylene, with the elastomeric PBEs having an ethylene content of from 10 to 15 wt percent ethylene.

5 As used herein, the term "extensible" refers to any nonwoven material which, upon application of a biasing force, is able to undergo elongation to at least about 50 percent strain and more preferably at least about 70 percent strain without experiencing catastrophic failure.

10 The nonwoven material of the present invention will preferably have a basis weight (weight per unit area) from 10 grams per square meter (gsm) to 100 gsm. The basis weight can also be from 15 gsm to 60 gsm, and in one embodiment it can be 20 gsm.

15 As used herein, the term "tensile strength" describes the peak force for a given basis weight when pulled in either the machine direction (MD) or cross direction (CD) of a nonwoven when pulled to break. The peak force may or may not correspond to the force at break or strain at break. "Elongation" unless otherwise specified, refers to the strain corresponding to the tensile strength.

20 A first aspect of the invention is a meltblown fabric which has a MD peak tensile force ( $F_{MD}$ ) measured in pounds per one inch width and normalized to 20 gsm basis weight, described by being greater than  $[-0.00143 \times \text{elongation (percent)} + 0.823]$  if elongation is between 20 to 675 percent. If elongation is greater than about 675 percent,  $F_{MD}$  is greater than about 0.1 pounds (lb). The meltblown fabric comprises at least one copolymer with at least about 50 weight percent of units derived from propylene and at least about 5 weight percent of units derived from a comonomer other than propylene.

25 The copolymer is a PBPE having  $MWD < 3.5$ , and having heat of fusion less than about 90 Joules/gm, preferably less than about 70 Joules/gm, more preferably less than about 50 Joules/gm. When ethylene is used as a comonomer, the PBPE has from 3 to 15 percent of ethylene, or from 5 to 14 percent of ethylene, or 9 to 12 percent ethylene, by weight of the propylene based elastomer or plastomer. Suitable propylene based elastomers and/or plastomers are taught in WO03/040442, which is hereby incorporated by reference in  
30 its entirety.

Of particular interest for use in the present invention are reactor grade PBPEs having  $MWD$  less than 3.5. It is intended that the term "reactor grade" is as defined in US Patent

6,010,588 and in general refers to a polyolefin resin whose molecular weight distribution (MWD) or polydispersity has not been substantially altered after polymerization.

Although the remaining units of the propylene copolymer are derived from at least one comonomer such as ethylene, a  $C_{4-20}$   $\alpha$ -olefin, a  $C_{4-20}$  diene, a styrenic compound and  
5 the like, preferably the comonomer is at least one of ethylene and a  $C_{4-12}$   $\alpha$ -olefin such as 1-hexene or 1-octene. Preferably, the remaining units of the copolymer are derived only from ethylene.

The amount of comonomer other than ethylene in the propylene based elastomer or  
plastomer is a function of, at least in part, the comonomer and the desired heat of fusion of  
10 the copolymer. If the comonomer is ethylene, then typically the comonomer-derived units  
comprise not in excess of about 15 wt percent of the copolymer. The minimum amount of  
ethylene-derived units is typically at least about 3, preferably at least about 5 and more  
preferably at least about 9, wt percent based upon the weight of the copolymer. If the  
polymer comprises at least one other comonomer other than ethylene, then the preferred  
15 composition would have a heat of fusion approximately in the range of a propylene-ethylene  
copolymer with 3 to 20 wt. percent ethylene. Though not intending to be bound by theory, it  
is thought that attaining approximately similar crystallinity and crystal morphology is  
necessary to achieve similar functionality of said polymers in a nonwoven.

The propylene based elastomer or plastomer of this invention can be made by any  
20 process, and includes copolymers made by Zeigler-Natta, CGC (Constrained Geometry  
Catalyst), metallocene, and nonmetallocene, metal-centered, heteroaryl ligand catalysis.  
These copolymers include random, block and graft copolymers although preferably the  
copolymers are of a random configuration. Exemplary propylene copolymers include  
Exxon-Mobil VISTAMAXX polymer, and propylene/ethylene elastomers and plastomers by  
25 The Dow Chemical Company.

The density of the propylene based elastomers or plastomers of this invention is  
typically at least about 0.850, can be at least about 0.860 and can also be at least about 0.865  
grams per cubic centimeter ( $g/cm^3$ ) as measured by ASTM D-792.

The weight average molecular weight ( $M_w$ ) of the propylene based elastomers or  
30 plastomers of this invention can vary widely, but typically it is between 10,000 and  
1,000,000 (with the understanding that the only limit on the minimum or the maximum  $M_w$   
is that set by practical considerations). For homopolymers and copolymers used in the

manufacture of meltblown fabrics, preferably the minimum Mw is about 20,000, more preferably about 25,000.

The polydispersity of the propylene based elastomers or plastomers of this invention is typically between 2 and 3.5. "Narrow polydispersity", "narrow molecular weight distribution", "narrow MWD" and similar terms mean a ratio ( $M_w/M_n$ ) of weight average molecular weight ( $M_w$ ) to number average molecular weight ( $M_n$ ) of less than about 3.5, can be less than about 3.0, can also be less than about 2.8, can also be less than about 2.5, and can also be less than about 2.3. Polymers for use in fiber applications typically have a narrow polydispersity. Blends comprising two or more of the polymers of this invention, or blends comprising at least one copolymer of this invention and at least one other polymer, may have a polydispersity greater than 4 although for spinning considerations, the polydispersity of such blends is still preferably between 2 and 4.

The PBPEs for use in the present invention ideally have an MFR of from 20 to 5000, g/10min, or alternatively 2000 g/10min. MFR for copolymers of propylene and ethylene and/or one or more  $C_4$ - $C_{20}$   $\alpha$ -olefms is measured according to ASTM D-1238, condition L (2.16 kg, 230 degrees C).

MFRs greater than about 250 were estimated according to the following correlation:

$$MFR = 9 \times 10^{18} M_w T^{3.3584}$$

Mw (grams per mole) was measured using gel permeation chromatography.

The PBPEs may advantageously be subjected to a chemically induced chain scissioning agent. Such materials are known to increase the MFR of the polymers and to reduce their molecular weight distribution (MWD), thereby improving performance in the meltblown process. In general, it is preferred that the reactor grade PBPE have an MFR between 1 to 100 g/10min, whereas after chain scission (if any) the PBPE will preferably have an MFR of from 50 to 5000 g/10 min. Suitable chain scissioning agents include peroxide and non-peroxide type free radical initiators. For many applications, non-peroxide type chain scissioning agents are preferred such as cyclic and open chain hydroxylamine esters. One particularly preferred chain scissioning agent is the family of compounds known as hydroxyl amine esters (US2003/02 16494 A1, hereby incorporated by reference). The peroxide process has been reported to suffer from problems such as discoloration, odor, or smoke, which can be reduced by using non-peroxide chain scissioning agents. Further, it

has been observed that using hydroxyl amine esters increases the long term thermal stability and light stability. In some applications it may be desirable to use more than one type of chain scissioning agent such as in combination with peroxides or free-radical agents.

In one preferred embodiment of this invention, the propylene based elastomers or  
5 plastomers are further characterized as having at least one of the following properties:  
(i)  $^{13}\text{C}$  NMR peaks corresponding to a regio-error at about 14.6 and about 15.7 ppm, the  
peaks of about equal intensity, (ii) a DSC curve with a  $T_{\text{me}}$  that remains essentially the same  
and a  $T_{\text{max}}$  that decreases as the amount of comonomer, that is, the units derived from  
ethylene and/or the unsaturated comonomer(s), in the copolymer is increased, and (iii) an X-  
10 ray diffraction pattern when the sample is slow-cooled that reports more gamma-form  
crystals than a comparable copolymer prepared with a Ziegler-Natta (Z-N) catalyst.  
Typically the copolymers of this embodiment are characterized by at least two, preferably all  
three, of these properties. In other embodiments of this invention, these copolymers are  
characterized further as also having one or both of the following characteristics: (iv) a B-  
15 value when measured according to the method of Koenig (described below) greater than  
about 1.03 when the comonomer content, that is, the units derived from the comonomer  
other than propylene, is at least about 3 wt percent, and (v) a skewness index,  $S_{ix}$ , greater  
than about -1.20. Each of these properties and their respective measurements are described  
in detail in USSN 10/139,786 filed May 5, 2002 (WO2/003040442) which is incorporated  
20 herein by reference, as supplemented below.

#### B-Value

"High B-value" and similar terms mean the ethylene units of a copolymer of  
propylene and ethylene, or a copolymer of propylene, ethylene and at least one unsaturated  
comonomer, is distributed across the polymer chain in a nonrandom manner. B-values  
25 range from 0 to 2. The higher the B-value, the more alternating the comonomer distribution  
in the copolymer. The lower the B-value, the more blocky or clustered the comonomer  
distribution in the copolymer. The high B-values of the polymers made using a  
nonmetallocene, metal-centered, heteroaryl ligand catalyst, such as described in U.S. Patent  
Publication No. 2003/0204017 A1, are typically at least about 1.03 as determined according  
30 to the method of Koenig (Spectroscopy of Polymers American Chemical Society,  
Washington, DC, 1992), preferably at least about 1.04, more preferably at least about 1.05  
and in some instances at least about 1.06. This is very different from propylene-based

copolymers typically made with metallocene catalysts, which generally exhibit B-values less than 1.00, typically less than 0.95. There are several ways to calculate B-value; the method described below utilizes the method of Koenig, J.L., where a B-value of 1 designates a perfectly random distribution of comonomer units. The B-value as described  
 5 by Koenig is calculated as follows.

B is defined for a propylene / ethylene copolymer as:

$$B = \frac{f(EP + PE)}{2 \cdot F_E \cdot F_P}$$

where  $f(EP + PE)$  = the sum of the EP and PE diad fractions; and  $F_e$  and  $F_p$  = the mole fraction of ethylene and propylene in the copolymer, respectively. The diad fraction can be  
 10 derived from triad data according to:  $f(EP + PE) = [EPE] + [EPP+PPE]/2 + [PEP] + [EEP+PEE]/2$ . The B-values can be calculated for other copolymers in an analogous manner by assignment of the respective copolymer diads. For example, calculation of the B-value for a propylene/ 1-octene copolymer uses the following equation:

$$B = \frac{f(OP + PQ)}{2 \cdot F_O \cdot F_P}$$

15 For propylene polymers made with a metallocene catalyst, the B-values are typically between 0.8 and 0.95. In contrast, the B-values of the propylene polymers made with an activated nonmetallocene, metal-centered, heteroaryl ligand catalyst (as described below), are above about 1.03, typically between 1.04 and 1.08. In turn, this means that for any propylene-ethylene copolymer made with such a nonmetallocene metal-centered, heteroaryl  
 20 catalyst, not only is the propylene block length relatively short for a given percentage of ethylene but very little, if any, long sequences of 3 or more sequential ethylene insertions are present in the copolymer, unless the ethylene content of the polymer is very high.

### <sup>13</sup>C NMR

The propylene ethylene copolymers suitable for use in this invention typically have  
 25 substantially isotactic propylene sequences. "Substantially isotactic propylene sequences" and similar terms mean that the sequences have an isotactic triad (mm) measured by <sup>13</sup>C NMR of greater than about 0.85, preferably greater than about 0.90, more preferably greater than about 0.92 and most preferably greater than about 0.93. Isotactic triads are well known in the art and are described in, for example, USP 5,504,172 and WO 00/01745 which

refer to the isotactic sequence in terms of a triad unit in the copolymer molecular chain determined by  $^{13}\text{C}$  NMR spectra. NMR spectra are determined as follows.

$^{13}\text{C}$  NMR spectroscopy is one of a number of techniques known in the art for measuring comonomer incorporation into a polymer. An example of this technique is described for the determination of comonomer content for ethylene/ $\alpha$ -olefin copolymers in Randall (Journal of Macromolecular Science, Reviews in Macromolecular Chemistry and Physics, C29 (2 & 3), 201 - 317 (1989)). The basic procedure for determining the comonomer content of an olefin interpolymer involves obtaining the  $^{13}\text{C}$  NMR spectrum under conditions where the intensity of the peaks corresponding to the different carbons in the sample is directly proportional to the total number of contributing nuclei in the sample. Methods for ensuring this proportionality are known in the art and involve allowance for sufficient time for relaxation after a pulse, the use of gated-decoupling techniques, relaxation agents, and the like. The relative intensity of a peak or group of peaks is obtained in practice from its computer-generated integral. After obtaining the spectrum and integrating the peaks, those peaks associated with the comonomer are assigned. This assignment can be made by reference to known spectra or literature, or by synthesis and analysis of model compounds, or by the use of isotopically labeled comonomer. The mole percent comonomer can be determined by the ratio of the integrals corresponding to the number of moles of comonomer to the integrals corresponding to the number of moles of all of the monomers in the interpolymer, as described in Randall, for example.

The data is collected using a Varian UNITY Plus 400MHz NMR spectrometer, corresponding to a  $^{13}\text{C}$  resonance frequency of 100.4 MHz. Acquisition parameters are selected to ensure quantitative  $^{13}\text{C}$  data acquisition in the presence of the relaxation agent. The data is acquired using gated  $^1\text{H}$  decoupling, 4000 transients per data file, a 7sec pulse repetition delay, spectral width of 24,200Hz and a file size of 32K data points, with the probe head heated to 130° C. The sample is prepared by adding approximately 3mL of a 50/50 mixture of tetrachloroethane-d<sub>2</sub>/orthodichlorobenzene that is 0.025M in chromium acetylacetonate (relaxation agent) to 0.4g sample in a 10mm NMR tube. The headspace of the tube is purged of oxygen by displacement with pure nitrogen. The sample is dissolved and homogenized by heating the tube and its contents to 150°C with periodic refluxing initiated by heat gun.

Following data collection, the chemical shifts are internally referenced to the mmmm pentad at 21.90 ppm. Isotacticity at the triad level (mm) is determined from the methyl integrals representing the mm triad (22.5 to 21.28 ppm), the mr triad (21.28-20.40 ppm), and the rr triad (20.67-19.4 ppm). The percentage of mm tacticity is determined by dividing the intensity of the mm triad by the sum of the mm, mr, and rr triads. For propylene-ethylene copolymers made with catalyst systems, such as the nonmetallocene, metal-centered, heteroaryl ligand catalyst (described above) the mr region is corrected for ethylene and regio-error by subtracting the contribution from PPQ and PPE. For propylene-ethylene copolymers the rr region is corrected for ethylene and regio-error by subtracting the contribution from PQE and EPE. For copolymers with other monomers that produce peaks in the regions of mm, mr, and rr, the integrals for these regions are similarly corrected by subtracting the interfering peaks using standard NMR techniques, once the peaks have been identified. This can be accomplished, for example, by analyzing a series of copolymers of various levels of monomer incorporation, by literature assignments, by isotopic labeling, or other means which are known in the art.

For copolymers made using a nonmetallocene, metal-centered, heteroaryl ligand catalyst, such as described in U.S. Patent Publication NO. 2003/0204017, the  $^{13}\text{C}$  NMR peaks corresponding to a regio-error at about 14.6 and about 15.7 ppm are believed to be the result of stereoselective 2,1-insertion errors of propylene units into the growing polymer chain. In general, for a given comonomer content, higher levels of regio-errors lead to a lowering of the melting point and the modulus of the polymer, while lower levels lead to a higher melting point and a higher modulus of the polymer.

Matrix Method for Calculation of B-Values according to Koenig, J.L.

For propylene/ethylene copolymers the following procedure can be used to determine the comonomer composition and sequence distribution. Integral areas are determined from the  $^{13}\text{C}$  NMR spectrum and input into the matrix calculation to determine the mole fraction of each triad sequence. The matrix assignment is then used with the integrals to yield the mole fraction of each triad. The matrix calculation is a linear least squares implementation of Randall's (Journal of Macromolecular Chemistry and Physics, Reviews in Macromolecular Chemistry and Physics, C29 (2&3), 201-317, 1989) method modified to include the additional peaks and sequences for the 2,1 regio-error. Table A shows the integral regions and triad designations used in the assignment matrix. The

numbers associated with each carbon indicate in which region of the spectrum it will resonate.

Mathematically the Matrix Method is a vector equation  $s = \beta M f$  where  $M$  is an assignment matrix,  $s$  is a spectrum row -vector, and  $f$  is a mole fraction composition vector.

5 Successful implementation of the Matrix Method requires that  $M$ ,  $f$ , and  $s$  be defined such that the resulting equation is determined or over determined (equal or more independent equations than variables) and the solution to the equation contains the molecular information necessary to calculate the desired structural information. The first step in the Matrix Method is to determine the elements in the composition vector/. The elements of

10 this vector should be molecular parameters selected to provide structural information about the system being studied. For copolymers, a reasonable set of parameters would be any odd  $n$ -ad distribution. Normally peaks from individual triads are reasonably well resolved and easy to assign, thus the triad distribution is the most often used in this composition vector/. The triads for the E/P copolymer are EEE, EEP, PEE, PEP, PPP, PPE, EPP, and EPE. For a

15 polymer chain of reasonable high molecular weight ( $\geq 10,000$  g/mol), the  $^{13}\text{C}$  NMR experiment cannot distinguish EEP from PEE or PPE from EPP. Since all Markovian E/P copolymers have the mole fraction of PEE and EPP equal to each other, the equality restriction was chosen for the implementation as well. Same treatment was carried out for PPE and EPP. The above two equality restrictions reduce the eight triads into six

20 independent variables. For clarity reason, the composition vector/ $f$  is still represented by all eight triads. The equality restrictions are implemented as internal restrictions when solving the matrix. The second step in the Matrix Method is to define the spectrum vector  $s$ . Usually the elements of this vector will be the well-defined integral regions in the spectrum. To insure a determined system the number of integrals needs to be as large as the number of

25 independent variables. The third step is to determine the assignment matrix  $M$ . The matrix is constructed by finding the contribution of the carbons of the center monomer unit in each triad (column) towards each integral region (row). One needs to be consistent about the polymer propagation direction when deciding which carbons belong to the central unit. A useful property of this assignment matrix is that the sum of each row should equal to the

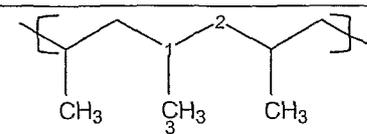
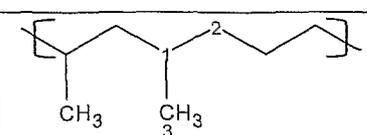
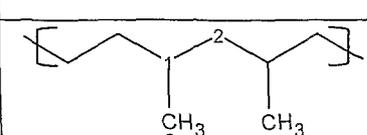
30 number of carbons in the center unit of the triad which is the contributor of the row. This equality can be checked easily and thus prevents some common data entry errors.

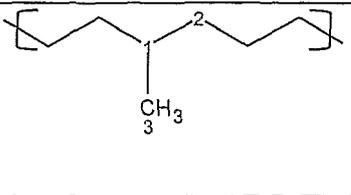
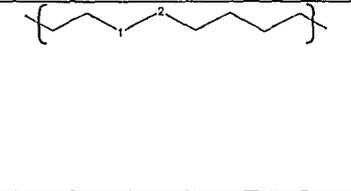
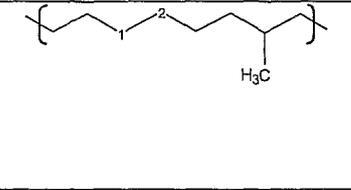
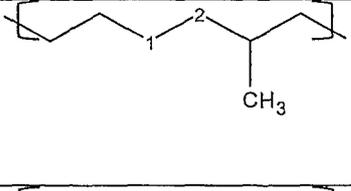
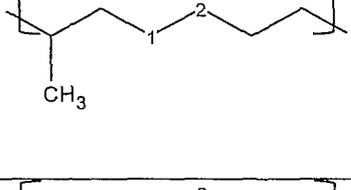
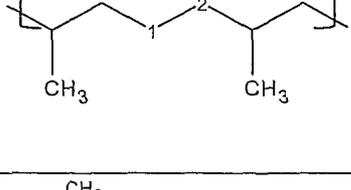
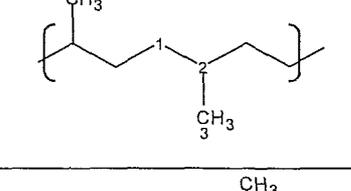
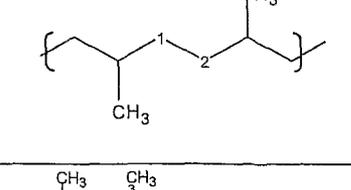
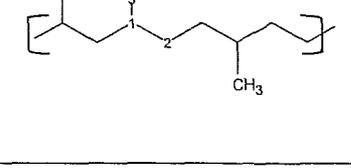
After constructing the assignment matrix, a redundancy check needs to be performed. In other words, the number of linearly independent columns needs to be greater or equal to the number of independent variables in the product vector. If the matrix fails the redundancy test, then one needs to go back to the second step and repartition the integral regions and then redefine the assignment matrix until the redundancy check is passed.

In general, when the number of columns plus the number of additional restrictions or constraints is greater than the number of rows in the matrix  $M$  the system is overdetermined. The greater this difference is the more the system is overdetermined. The more overdetermined the system, the more the Matrix Method can correct for or identify inconsistent data which might arise from integration of low signal to noise (S/N) ratio data, or partial saturation of some resonances.

The final step is to solve the matrix. This is easily executed in Microsoft Excel by using the Solver function. The Solver works by first guessing a solution vector (molar ratios among different triads) and then iteratively guessing to minimize the sum of the differences between the calculated product vector and the input product vector  $s$ . The Solver also lets one input restrictions or constraints explicitly.

**Table A.** The contribution of each carbon on the central unit of each triad towards different integral regions. P=propylene, E=ethylene., Q=2,1 inserted propylene.

Triad name	Structure	Region for 1	Region for 2	Region for 3
PPP		L	A	O
PPE		J	C	O
EPP		J	A	O

EPE		H	C	O
EEEE		K	K	
EEEP		K	J	
EEP		M	C	
PEE		M	J	
PEP		N	C	
PQE		F	G	O
QEP		F	F	
XPPQE		J	F	O

XPPQP		J	E	O
PPQPX		I	D	Q
PQPPX		F	B	P

**Chemical Shift Ranges**

	A	B	C	D	E	F	G	H	I
	48.00	43.80	39.00	37.25	35.80	35.00	34.00	33.60	32.90
	45.60	43.40	37.30	36.95	35.40	34.50	33.60	33.00	32.50
5	J	K	L	M	N	O	P	Q	
	31.30	30.20	29.30	27.60	25.00	22.00	16.00	15.00	
	30.30	29.80	28.20	27.10	24.50	19.50	15.00	14.00	

1,2 inserted propylene composition is calculated by summing all of the stereoregular propylene centered triad sequence mole fractions. 2,1 inserted propylene composition (Q) is calculated by summing all of the Q centered triad sequence mole fractions. The mole percent is calculated by multiplying the mole fraction by 100. C2 composition is determined by subtracting the P and Q mole percentage values from 100.

DSC Method

Differential scanning calorimetry (DSC) is a common technique that can be used to examine the melting and crystallization of semi-crystalline polymers. General principles of DSC measurements and applications of DSC to studying semi-crystalline polymers are described in standard texts (for example, E. A. Turi, ed., *Thermal Characterization of Polymeric Materials*, Academic Press, 1981). Certain of the copolymers used in the practice of this invention are characterized by a DSC curve with a  $T_{me}$  that remains essentially the same and a  $T_{ma}\chi$  that decreases as the amount of unsaturated comonomer in the copolymer is increased.  $T_{me}$  means the temperature at which the melting ends.  $T_{max}$  means the peak melting temperature.

Differential Scanning Calorimetry (DSC) analysis is determined using a model Q1000 DSC from TA Instruments, Inc. Calibration of the DSC is done as follows. First, a baseline is obtained by running the DSC from  $-90^{\circ}\text{C}$  to  $290^{\circ}\text{C}$  without any sample in the aluminum DSC pan. Then 7 milligrams of a fresh indium sample is analyzed by heating the sample to  $180^{\circ}\text{C}$ , cooling the sample to  $140^{\circ}\text{C}$  at a cooling rate of  $10^{\circ}\text{C}/\text{min}$  followed by keeping the sample isothermally at  $140^{\circ}\text{C}$  for 1 minute, followed by heating the sample from  $140^{\circ}\text{C}$  to  $180^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . The heat of fusion and the onset of melting of the indium sample are determined and checked to be within  $0.5^{\circ}\text{C}$  from  $156.6^{\circ}\text{C}$  for the onset of melting and within  $0.5\text{ J/g}$  from  $28.71\text{ J/g}$  for the heat of fusion. Then deionized water is analyzed by cooling a small drop of fresh sample in the DSC pan from  $25^{\circ}\text{C}$  to  $-30^{\circ}\text{C}$  at a cooling rate of  $10^{\circ}\text{C}/\text{min}$ . The sample is kept isothermally at  $-30^{\circ}\text{C}$  for 2 minutes and heated to  $30^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . The onset of melting is determined and checked to be within  $0.5^{\circ}\text{C}$  from  $0^{\circ}\text{C}$ .

The polypropylene samples are pressed into a thin film at a temperature of  $190^{\circ}\text{C}$ . About 5 to 8 mg of sample is weighed out and placed in the DSC pan. The lid is crimped on the pan to ensure a closed atmosphere. The sample pan is placed in the DSC cell and the heated at a high rate of about  $100^{\circ}\text{C}/\text{min}$  to a temperature of about  $60^{\circ}\text{C}$  above the melt temperature. The sample is kept at this temperature for about 3 minutes. Then the sample is cooled at a rate of  $10^{\circ}\text{C}/\text{min}$  to  $-40^{\circ}\text{C}$ , and kept isothermally at that temperature for 3 minutes. The sample is subsequently heated at a rate of  $10^{\circ}\text{C}/\text{min}$  until complete melting. The resulting enthalpy curves are analyzed for peak melt temperature, onset and peak crystallization temperatures, heat of fusion and heat of crystallization,  $T_{\text{me}}$ , and any other DSC analyses of interest.

Mechanical testing was performed using an Instron (Model 5564) sourced from Instron Corporation (Norwood, MA) and equipped with a 100 N load cell. This instrument was used for the tensile test and the 50 percent hysteresis test described below.

#### Skewness index

The skewness index is calculated from data obtained from temperature-rising elution fractionation (TREF). The data is expressed as a normalized plot of weight fraction as a function of elution temperature. The separation mechanism is analogous to that of copolymers of ethylene, whereby the molar content of the crystallizable component (ethylene) is the primary factor that determines the elution temperature. In the case of

copolymers of propylene, it is the molar content of isotactic propylene units that primarily determines the elution temperature.

The shape of the metallocene curve arises from the inherent, random incorporation of comonomer. A prominent characteristic of the shape of the curve is the tailing at lower elution temperature compared to the sharpness or steepness of the curve at the higher elution temperatures. A statistic that reflects this type of asymmetry is skewness. The equation below mathematically represents the skewness index,  $S_{ix}$ , as a measure of this asymmetry.

$$S_{ix} = \frac{\sqrt[3]{\sum w_i * (T_i - T_{Max})^3}}{\sqrt{\sum w_i * (T_i - T_{Max})^2}}$$

10

The value,  $T_{max}$ , is defined as the temperature of the largest weight fraction eluting between 50 and 90°C in the TREF curve.  $T_i$  and  $w_i$  are the elution temperature and weight fraction respectively of an arbitrary,  $i^{th}$  fraction in the TREF distribution. The distributions have been normalized (the sum of the  $w_i$  equals 100 percent) with respect to the total area of the curve eluting above 30°C. Thus, the index reflects only the shape of the crystallized polymer. Any uncrystallized polymer (polymer still in solution at or below 30°C) has been omitted from the calculation shown in Equation 1.

15

#### Gel Permeation Chromatography

Molecular weight distribution of the polymers is determined using gel permeation chromatography (GPC) on a Polymer Laboratories PL-GPC-220 high temperature chromatographic unit equipped with four linear mixed bed columns (Polymer Laboratories (20-micron particle size)). The oven temperature is at 160°C with the autosampler hot zone at 160°C and the warm zone at 145°C. The solvent is 1,2,4-trichlorobenzene containing 200 ppm 2,6-di-*t*-butyl-4-methylphenol. The flow rate is 1.0 milliliter/minute and the injection size is 100 microliters. About 0.2 percent by weight solutions of the samples are prepared for injection by dissolving the sample in nitrogen purged 1,2,4-trichlorobenzene containing 200 ppm 2,6-di-*t*-butyl-4-methylphenol for 2.5 hrs at 160°C with gentle mixing.

25

The molecular weight determination is deduced by using ten narrow molecular weight distribution polystyrene standards (from Polymer Laboratories, EasiCal PSI ranging from 580 - 7,500,000 g/mole) in conjunction with their elution volumes. The equivalent polypropylene molecular weights are determined by using appropriate Mark-Houwink

30

coefficients for polypropylene (as described by Th.G. Scholte, N.L.J. Meijerink, H.M. Schoffeleers, and A.M.G. Brands, J. Appl. Polym. Sci., 29, 3763 - 3782 (1984)) and polystyrene (as described by E. P. Otocka, R. J. Roe, N. Y. Hellman, P. M. Muglia, Macromolecules, 4, 507 (1971)) in the Mark-Houwink equation:

5 
$$\{N\} = KM^a$$

where  $K_{pp} = 1.90E-04$ ,  $a_{pp} = 0.725$  and  $K_{ps} = 1.26E-04$ ,  $a_{ps} = 0.702$ .

The meltblown fabrics of the present invention may be made with 100 percent PBPE or can be blended with other polymers to form the fibers used to make the fabric. Suitable  
10 polymers for blending with these PBPEs are commercially available from a variety of suppliers and include, but are not limited to, other polyolefins such as an ethylene polymer (for example, low density polyethylene (LDPE), ULDPE, medium density polyethylene (MDPE), LLDPE, HDPE, homogeneously branched linear ethylene polymer, substantially linear ethylene polymer, graft-modified ethylene polymer, ethylene-styrene interpolymers  
15 (ESI), ethylene vinyl acetate interpolymer, ethylene acrylic acid interpolymer, ethylene ethyl acetate interpolymer, ethylene methacrylic acid interpolymer, ethylene methacrylic acid ionomer, and the like), polycarbonate, polystyrene, conventional polypropylene (for example, homopolymer polypropylene, polypropylene copolymer, random block polypropylene interpolymer and the like), thermoplastic polyurethane, polyamide, polylactic  
20 acid interpolymer, thermoplastic block polymer (for example styrene butadiene copolymer, styrene butadiene styrene triblock copolymer, styrene ethylene-butylene styrene triblock copolymer and the like), polyether block copolymer (for example, PEBAX), copolyester polymer, polyester/polyether block polymers (for example, HYTEL), ethylene carbon monoxide interpolymer (for example, ethylene/carbon monoxide (ECO), copolymer,  
25 ethylene/acrylic acid/carbon monoxide (EAACO) terpolymer, ethylene/methacrylic acid/carbon monoxide (EMAACO) terpolymer, ethylene/vinyl acetate/carbon monoxide (EVACO) terpolymer and styrene/carbon monoxide (SCO)), polyethylene terephthalate (PET), chlorinated polyethylene, and the like and mixtures thereof. If the PBPE (or blend of  
30 PBPEs) used to make the meltblown fabric of the present invention is blended with one or more other polymers, then the PBPE(s) preferably comprises at least about 90, more preferably at least about 92 and more preferably at least about 94 and more preferably at least about 96 wt percent of the total weight of the blend.

It should also be readily recognized that other additives might also be added as is generally known in the art. Examples of such additives include antioxidants, ultraviolet light stabilizers, thermal stabilizers, slip agents, pigments or colorants, processing aids (such as fluoropolymers), crosslinking catalysts, flame retardants, fillers, foaming agents, etc.

5 Slip agents or antistatic agents may be particularly beneficial when the PBPE used to make the meltblown fabric contains more than about 9 wt percent ethylene, as it was observed that such fabrics tended to stick to the collecting drum or belt making it difficult to remove. Typical slip agents include oleicamide, erucamide, or stearicamide, and a typical antistatic agent is glycerol mono stearate (GMS).

10 The meltblown fabric can be made in any manner known in the art. Typical processes include but are not limited to the Exxon single-row type line, the multirow Biax-Fiberfilm, and the Hills type line. Description of nonwoven processes are described in the respective art of the respective companies and in publications such as *The Nonwovens Handbook*, Association of Nonwovens Fabrics Industry, Cary NC and Principles of  
15 Nonwovens, INDA, Cary NC. U.S. Pat. No. 3,849,241 also describes a suitable meltblown process. These references are hereby incorporated by reference.

The meltblown fabrics of the present invention will have a tensile strength ( $F_{MD}$ ) of greater than about  $[-0.00143 \times \text{elong}(\text{percent}) + 0.823]$  if elongation (denoted by  $\text{elong}(\text{percent})$ ) is between 20 to 675 percent and greater than about 0.1 lb if elongation is  
20 greater than or equal to 675 percent per one inch width (normalized to 20 gsm).

Tensile strength is peak force on a normalized basis to 20 gsm. This is calculated according to the following equation:

$$F_{MD} = F_{Peak,MD} \times \frac{20}{BasisWt(gsm)}$$

such that  $F_{Peak,MD}$  is the peak force measured for a 1 inch wide by 6 inch long strip cut  
25 parallel to the machine direction which is gripped by line contact grips with a spacing of 3 inches. The sample is pulled to break at a rate of 10 inches per minute. The resulting  $F_{MD}$  is measured in pounds per 1 inch width. BasisWt is the basis weight of the nonwoven measured in grams per square meter. Basis weight is measured for each specimen by weighing the 1 inch wide by 6 inch long sample strips on a analytical balance and  
30 converting to grams per square meter. Care is taken to avoid sampling from the edges and

defects present in the web. Defects comprise holes, nonuniform sections, and fiber aggregations.

More preferably the meltblown fabrics of the present invention will have a tensile strength of greater than  $[-0.00143 \times \text{elong}(\text{percent}) + 1]$  and even more preferably greater than  $[-0.00143 \times \text{elong}(\text{percent}) + 1.2]$  per one inch width (normalized to 20 gsm) for elongation of 20 to 675 percent strain. Elongation was defined according to the following equation:

$$\text{Elongation}(\%) = \frac{L_{\text{peak force}} - L_0}{L_0} \times 100\%$$

such that  $L_0$  is the initial length of three inches, and  $L_{\text{peak force}}$  is the length corresponding to the strain at the  $F_{\text{Peak MD}}$ . Strain is defined as the percent change in length of the sample.

$$\text{Strain}(\%) = \frac{L - L_0}{L_0} \times 100\%$$

such that  $L$  is the length of the sample.

The meltblown fabric of the present invention also preferably has immediate set of less than or equal to about 35 percent or more preferably less than or equal to about 12 percent as measured by a 50 percent hysteresis test. The 50 percent hysteresis test is carried out as follows: a 1 inch wide by 6 inch long strip cut parallel to the machine direction which is gripped by line contact grips with a spacing of 3 inches. The sample is pulled to a strain of 50 percent strain at a rate of 10 inches per minute. The crosshead is then immediately returned at the same rate until 0 percent strain. The crosshead is then immediately extended again at the same rate until a positive tensile force is measured. This point is defined as permanent set. The strain corresponding to the onset of the positive force is taken as the immediate set strain.

Further, the meltblown fabric of the present invention preferably has retained load greater than or equal to about 0 percent or even more preferably greater than or equal to about 20 percent as measured by a 50 percent hysteresis test. Retained load is measured as the force at 30 percent strain during retraction divided by the force at 30 percent strain during the first extension. Retained load is taken as this ratio multiplied by 100 percent.

### Hydrohead

Hydrohead is measure according to EDANA test method: WSP 80.6(05)/. The test method applies to nonwoven fabrics, which are intended for use as a barrier to penetrating fluids. The hydrostatic pressure test measures the resistance of nonwoven fabrics to the penetration of water under varied hydrostatic head pressures.

The nonwoven fabric is mounted to form the cover on the test head reservoir. The specimen is subjected to a standardized water pressure and a constant rate until leakage appears on the outer surface of the nonwoven. The test results for the hydrostatic water pressure test are measured at the point where the first drops of appear in three separate areas on the specimen. Results are reported in either centimeters/minute or millibars/minute.

The preferred meltblown nonwoven fabrics will have hydrohead performance from 10, preferably 20 to 80 cm H<sub>2</sub>O/min for a 25 gsm basis weight. Higher basis weights may be able to achieve higher hydrohead performance.

### LAMINATE STRUCTURES

In many applications, the meltblown fabrics, such as those of the present invention, can be improved upon by combining the meltblown fabric with one or more additional fabric layers bonded together. Such structures are often identified by letters designating the various lays such as SM for a two layer structure consisting of a spunbond layer and a meltblown layer, SMS for a three layer structure, or more generically SM<sub>x</sub>S structures (x is the number of meltblown layers). Laminate structures, particularly those comprising the above-described meltblown layers, is another aspect of the present invention.

The nonwoven laminates of the present invention comprise at least two nonwoven layers. It is preferred that at least one of the nonwoven layers be made using the meltblown process, and at least one of the nonwoven layers be made using the spunbond process. The nonwoven laminates of the present invention will be characterized by their combination of overall structure softness and bonding strength between the layers.

Bending modulus is determined by ASTM D 5732-95. The preferred nonwoven laminates of the present invention will have an overall normalized bending modulus ( $E_{\text{bend}} \cdot MD^{-20}_{\text{gsm}}$ ) less than 0.06 mN-cm more preferably less than 0.04 mN-cm and most preferably less than 0.03 mN-cm for a normalized basis weight of 20 gsm. This is calculated according to the following formula:

$$E_{\text{bend},ME,20\text{gsm}} = E_{\text{bend},MD} \times \frac{20}{\text{BasisWt}(gsm)}$$

such that  $E_{\text{bend},MD}$  is the as measured bending modulus and  $\text{Basis Wt}$  is the basis weight of the fabric measured in grams per square meter.

The preferred nonwoven laminates will also exhibit a peel strength between the nonwoven layers of more than about 2 N/5cm, more preferably greater than about 2.5N/5cm and most preferably greater than 3N/5cm. Peel strength is determined by the maximum force in N required to peel two or more substrates apart from each other using a specimen with a width of 5cm.

The two nonwoven layers may be made of any polymer or polymer blend capable of forming a nonwoven laminate structure having an overall bending modulus of about 0.005 N-mm or less and a peel strength between the nonwoven layers of at least about 2 N/5cm. It is generally preferred that at least one nonwoven layer be a meltblown layer, with the above-described meltblown nonwoven fabrics being particularly preferred. Other meltblown fabrics which may be suitable for these novel laminates include but are not limited to those described in US 2005/0 106978 and WO 2005/052052.

It is generally preferred that at least one of the layers be a spunbond layer and that this spunbond layer be made from fibers which comprise a polyethylene material. The fiber may be monofilament or a bicomponent fiber. Bicomponent fibers include all of the known configurations including sheath-core, side by side, and islands in the sea configurations. The sheath core fiber is the preferred bicomponent fiber configuration.

The spunbond fiber may be made from any suitable material. Specific embodiments include propylene based polymers, blends containing propylene based polymers, ethylene based polymers, blends containing ethylene based polymers, and blends thereof. Sometimes, improved softness is desired. Embodiments that meet this need include the spunbond fabrics described in recently filed US applications 11/083891 and 11/068098 (both or which are hereby incorporated by reference in their entirety), and spunbond fiber that comprises a polyethylene material particularly where the polyethylene material comprises at least a portion of the fiber's surface. "Polyethylene material" is meant to include any polymer comprising more than fifty mole percent ethylene. In many cases, the polymer will include an alpha olefin copolymer and typically that copolymer will be a C<sub>3</sub>-C<sub>20</sub> alpha olefin. Hexene and octene are preferred copolymers. The polyethylene material

can be made via gas-phase, solution-phase or slurry polymerization or any combination thereof, using any type of reactor or reactor configuration known in the art.

"Polyethylene material" includes many types of material known in the art, such as the materials known as low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) and blends containing such materials. Particularly useful polyethylene materials for use in the spunbond materials of the present invention are the LLDPE materials. This includes the substantially linear ethylene polymers which are further defined in U.S. Patent 5,272,236, U.S. Patent 5,278,272, U.S. Patent 5,582,923 and US Patent 5,733,155; the homogeneously branched linear ethylene polymer compositions such as those in U.S. Patent No. 3,645,992; the heterogeneously branched ethylene polymers such as those prepared according to the process disclosed in U.S. Patent No. 4,076,698; and/or blends thereof (such as those disclosed in US 3,914,342 or US 5,854,045). Each of these references is incorporated herein by reference.

The preferred laminate structures can have hydrohead performance from 100, preferably 200 to 800 mm H<sub>2</sub>O for a 25 gsm basis weight. Higher basis weights may be able to achieve higher hydrohead performance.

#### Additional Measurement Methods -

Unless otherwise indicated, the following analytical techniques are used to characterize the materials discussed in the present application.

#### Density Method:

Coupon samples (1 inch x 1 inch x 0.125 inch) were compression molded at 190°C according to ASTM D4703-00 and cooled using procedure B. Once the sample cooled to 40-50°C, it was removed. Once the sample reached 23°C, its dry weight and weight in isopropanol was measured using an Ohaus AP2 10 balance (Ohaus Corporation, Pine Brook NJ). Density was calculated as prescribed by ASTM D792 procedure B.

#### Tensile Test

A 1 inch wide by 6 inch long strip cut parallel to the machine direction which is gripped by line contact grips, separated by 3 inches. The flat grip facing is coated with rubber. Pressure is adjusted to prevent slippage (usually 50-100 psi). The crosshead is increased at 10 inches per minute until the specimen breaks. Strain is calculated by dividing the crosshead displacement by 3 inches and multiplying by 100. Load equals pounds force per 1 inch width.

Tensile strength is defined according to the following equation:

$$F_{MD} = F_{Peak,MD} \times \frac{2.0}{BasisWt(gsm)}$$

such that  $F_{Peak,MD}$  is the peak force measured according to the method described above and BasisWt is the basis weight of the nonwoven measured in grams per square meter.

5 Elongation was defined according to the following equation:

$$Elongation(\%) = \frac{L_{peakforce} - L_0}{L_0} \times 100$$

such that  $L_0$  is the initial length of three inches, and  $L_{peakforce}$  is the length corresponding to the strain at the  $F_{Peak,MD}$ .

#### Scanning Electron Microscopy:

10 Samples for scanning electron microscopy were mounted on aluminum sample stages with carbon black filled tape and copper tape. The mounted samples were then coated with 100-200 Å of gold using an SPI-Module Sputter Coater (Model Number 11430) from Structure Probe Incorporated (West Chester, Massachusetts) fitted with an argon gas supply and a vacuum pump.

15 The gold coated samples were then examined in a Hitachi S4100 scanning electron microscope equipped with a field effect gun and supplied by Hitachi America, Ltd (Shaumburg, Illinois). Samples were examined using secondary electron imaging mode were measured using an acceleration voltage of 3-5 kV and collected using a digital image capturing system.

20 Fiber diameters were measured by acquiring the images of the fabrics in at least three different locations. The diameters of at least 15 fiber diameters were measured from the images using ImagePro Express image analysis software (Media Cybernetics, Silver Spring MD). Care was taken not to measure the same fiber more than once and not to include measurements of "married" or "roped" filaments (fibers that were extensively  
25 bonded along the fiber axis). The average and standard deviation of the fiber diameters were then calculated.

#### SPECIFIC EMBODIMENTS

The effect of spinning conditions was examined for polymers with 25-38 MFR. Elongational stresses achieved by controlling throughput and take-off rate determined the  
30 amount of stress-induced crystallinity in the fiber and hence the resulting mechanical

properties. Higher elongational stresses achieved at a draw down greater than 1000 resulted in higher crystallinity and hence more rigid fibers. More elasticity was preserved at lower crystallinity or draw down less than 1000. For more elastic fiber, very low crystallinity or draw down less than 500 was preferred. To verify that elasticity was maintained, the tensile hysteresis behavior was measured.

The different resins used are presented in Tables 1 and 2. The process conditions used to synthesize the propylene-ethylene resins A, B, C, and D are shown in Table 1.

TABLE 1  
PROPYLENE-ETHYLENE RESIN PROCESS CONDITIONS

Resin	POLY VISE. CPOISE	POLY DENS G/CC	POLY PROD LB/HR	SOLV FLOW LB/HR	C <sub>3</sub> FLOW PPH	C <sub>2</sub> FLOW PPH	H <sub>2</sub> FLOW SCCM	MONO M CONV %	CONTRL TEMP DEGC	CATMTL EFF. MW#
A	73,151	0.8872	4.5	23.1	7.0	0.3	57.2	61.4	105.0	242,849
B	16,855	0.8761	4.7	23.1	7.0	0.5	117.6	60.9	105.0	274,579
C	68,009	0.8669	4.7	23.1	7.0	0.4	88.4	60.2	105.0	276,983
D	16,720	0.8661	4.9	23.1	7.0	0.6	143.6	60.8	105.0	312,893

The characteristics of the resins are listed in Table 2.

TABLE 2  
RESINS

Rasin	Description	Density (g/cc)	Ethylene Content (wt%)	MWD	Viscosity (190°C, cP)	MFR <sup>a</sup> (g/10min)
A	propylene-ethylene plastomer	0.8869	4.5	2.5	72650	233 <sup>a</sup>
B	propylene-ethylene plastomer	0.8770	8.3	2.3	15900	1059 <sup>o</sup>
C	propylene-ethylene elastomer	0.8649	10.5	2.5	71150	238 <sup>a</sup>
D	propylene-ethylene elastomer	0.8667	11.0	2.3	14700	1145 <sup>a</sup>
F	polypropylene homopolymer	0.902	0.0	n/a	n/a	U00 <sup>b</sup>
G	polypropylene homopolymer	0.902	0.0	n/a	n/a	350 <sup>b</sup>
H	propylene-ethylene plastomer	0.888	5	n/a	n/a	25
I	propylene-ethylene plastomer	0.876	9	n/a	n/a	25
J	propylene-ethylene elastomer	0.865	12	n/a	n/a	25
P	polypropylene-homopolymer (peroxide vise broken)	0.902	0	n/a	n/a	25
S	polypropylene-homopolymer	0.902	0	n/a	n/a	25

Resin	Description	Density (g/cc)	MI, g/10min <sup>b</sup>
K	ethylene -hexene copolymer	0.933	150
L	ethylene-octene copolymer	0.874	500
Q	Linear Low Density Polyethylene	0.950	17
R	Enhanced Polyethylene resin	0.936	20

<sup>a</sup> ASTM D-1238 (230°C, 2.16 kg)

<sup>b</sup> ASTM D-1238 (190°C, 2.16 kg)

Density was measured according to ASTM D-792. Ethylene content was measured using the NMR method described previously. Molecular weight distribution (MWD) was measured using the GPC method described above. Melt flow rate (MFR) was measured according to ASTM D-1238, condition L (2.16 kg, 230 degrees C).

5 Propylene-ethylene copolymers comprising 4.5-12.0 wt. percent ethylene were used. For comparison, an ethylene-octene copolymer and a polypropylene homopolymer were also used. The melt flow ratio (MFR) of the propylene-ethylene polymers was 25-145 g/10min. The melt index (MI) of the ethylene-based resins K and L were 150 and 500 g/10min, respectively.

10 Inventive and comparative examples were made using a Biax Fiber-Film meltblown line (Greenville, Wisconsin) with a variety of conditions. The spinneret had 128 holes (2 rows of 64 spinnerets), each of which had a diameter of 0.014 inches. The length to diameter ratio (L/D) for the 1 inch extruder was 20. In addition to extruder selection and die selection, the main variables were melt temperature, air pressure, air temperature,  
15 throughput (grams/hole/minute or ghm) which was controlled by pump speed, collector drum speed, die-to-collector distance (DCD). Selected inventive and comparative examples were also made on a Hills type meltblown line.

The conditions used to fabricate the inventive and comparative examples are shown in Tables 3, 4, and 5. By adjusting the variables described above, fiber diameter, basis  
20 weight, and the degree of self-bonding was controlled. Samples with only the number and hyphen designation (that is 1-1 to 6-4 and 7-1 to 9-1) are the inventive examples, and samples with the designation ending in the letter V (that is 1-lc to 3-3c) are the comparative examples.

25

**TABLE 3**  
**FABRIC EXAMPLES**

Ex	Resin	Melt Temp CQ	Air Pressure (psi)	Air Temp CQ	Throughput (ghm)	Collector Speed (ft/mm)	DCD (cm)	Basis Weight (gsm)
1-1	A	250	14	250	0.09	15	22	22.2
1-2	A	250	14	250	0.09	15	11	22.3
1-3	A	250	12	250	0.05	8	22	18.8
1-4	A	250	12	250	0.05	9	13.5	21.1
1-5	A	280	13	280	0.10	17	13.5	24.1
1-6	A	284	6	284	0.05	9	13.5	15.2
1-7	A	310	13	310	0.07	24	13.5	21.6
1-8	A	310	9	310	0.05	9	13.5	20.4
2-1	B	247	6.2	245	0.13	8.5	23	44.5
2-2	B	247	4	245	0.06	8	23	23.5
2-3	B	247	6.2	245	0.13	32	23	11.8
3-1	C	250	16	250	0.10	15.5	20	27.7
3-2	C	250	-	-	-	-	-	25.6
3-3	C	275	7.5	275	0.03	6	21	21.5
3-4	C	275	11	275	0.09	15	21	19.2
4-1	D	250	8	250	0.18	25	25	34.0
4-2	D	250	4	250	0.06	9	25	23.7
4-3	D	250	6	250	Oil	18	25	24.9
5-1	90/10 B/F	247	6	255	Oil	19	23	24.1
5-2	90/10 B/F	247	6	255	0.05	8.5	23	16.6
5-3	90/10 B/F	270	7	255	0.13	2.1	23	25.1
6-1	75/25 C/G	250	4	250	0.12	20	22	22.9
6-2	75/25 C/G	250	4	250	0.12	20	10	26.6
6-3	75/25 C/G	280	5	280	0.12	20	22	25.3
6-4	75/25 C/G	280	5	280	0.12	20	10	26.7
1-1c	F	290	4	285	-	8.5	10	22.6
1-2c	F	290	6.2	285	-	17.4	10	23.0
1-3c	F	290	9.8	285	-	25.7	10	23.3
1-4c	F	247	8	245	-	8	10	22.5
1-5c	F	247	9	245	-	16	10	20.4
1-6c	F	247	12	245	-	24.4	10	19.8
2-1c	K	280	10	280	Oil	16	10	23.4
2-2o	K	280	10	280	<b>Oil</b>	16	5	21.8
2-3c	K	280	10	280	<b>Oil</b>	16	5	24.2
2-4c	K	314	4	310	<b>Oil</b>	16	5	23.6
3-1c	L	250	7	250	0.15	25	20	23.0
3-2c	L	220	8	220	0.12	19	20	20.4
3-3c	L	220	4	220	0.04	7	20	20.9
7-1c	F	252	696	275	55	29	150	25.1
8-1c	98.5/1.5 G/X	262	697	276	5.1	29	150	23.0
9-1	97.5/2.5 H/X	255	407	275	48	34	330	21.7

The letter "c" in the designation denotes comparative example

X is IRGATEC CR76 polymer modifier available from Ciba Specialty Chemicals, which is a hydroxyl amine ester in a masterbatch

5

Samples 7-1, 8-1, 9-1 were made on a Hills type line. All others in this table were made with Biax 5" width meltblown line manufactured by the Biax-Fiberfilm Corporation (Greenville, Wisconsin, USA)

Fabric samples made to examine the effect of hydroxylamine masterbatch level were made. They are described in Table 4.

TABLE 4  
FABRIC EXAMPLES MADE WITH MODIFIED RESINS

Ex.	Resin	X (wt.%)	Melt Temp (°C)	Screw Speed (rpm)	Throughput (ghm)	Mw (g/mol)	MFR <sup>a</sup> (g/10 min)
10-01	H	1.5	250	20	0.13	74500	390
10-02	J	1.5	280	20	0.15	55500	1050
10-03	J	1.5	280	20	0.12	52600	1257
10-04	I	3	280	20	-	54200	1137
10-05	I	3	250	20	0.12	75 100	380
10-06	J	1.5	250	20	-	65700	596
10-07	J	1.5	250	20	-	72800	422
10-08	I	1.5	250	20	-	72200	434
10-09	I	1.5	280	20	-	59200	845
10-10	J	3	250	20	0.08	50600	1432
10-11	J	3	230	20	0.14	83300	268

<sup>a</sup>ASTMD-1238 (230°C, 2.16 kg)

5

Further examples of fabrics made on the Hills type line are described in Table 5. Notice that the hydrohead performance of these novel fabrics are comparable to conventional hPP-based fabrics while imparting the additional desirable bonding performance.

10

TABLE 5  
FABRIC EXAMPLES

Example	Resin	Fabric Weight (g/m <sup>2</sup> )	Hydrohead (mm)
U-OIc	S	25	700
11-02c	S	35	882
H-O <sub>3</sub> C	S	50	1017
11-04c	98.5/1.5 P/X	25	295
11-05c	98.5/1.5 P/X	35	282
11-06c	98.5/1.5 P/X	50	532
11-07c	98.5/1.5 P/X	25	330
11-08c	98.5/1.5 P/X	35	497
11-09	98.5/1.5 H/X	50	402
11-10	98.5/1.5 H/X	25	365
11-11	98.5/1.5 H/X	35	542
11-12	98.5/1.5 H/X	50	480
n-i3	98.5/1.5 H/X	20+6+6	300; 333
11-14	J	25	n/a
11-15	J	50	n/a
11-16	J	100	n/a
11-17c	S	139	380; 510
11-18c	F	25	n/a
11-19	97.5/2.5 H/X	25	n/a

The letter 'c' in the designation denotes a comparative example.

By plotting the bending moduli against elongation of the fabrics described in the preceding tables (Figure 1), the differentiation of the inventive fibers and the comparative examples is evident. Inventive fibers describe a region of higher elongation (greater than about 75 percent) and lower normalized modulus (less than 0.6 mN-cm at 20 gm) in contrast to the comparative examples. Functionally, this behavior translates to fibers that can exhibit better drape (lower bending modulus) and fibers that can have greater extensibility (higher elongation to break).

Figure 2 shows the normalized peak force plotted against elongation to break. In contrast to the comparative examples, the inventive samples occupy a region of higher peak force and elongation described by the equations:

a.  $F_{MD} \geq [-0.00143 \times \text{elong}(\text{percent}) + 0.823]$  if elongation is between 20 to 675 percent strain.

b.  $F_{MD} \geq 0.1$  lb if elongation is greater than or equal to 675 percent strain.

This result combined with the result from Figure 1 demonstrates that the inventive examples exhibit the novel and desirable combination of the following properties: better drape (lower bending modulus), higher extensibility (higher elongation at peak force), and higher strength (higher normalized peak force).

There are various aspects of elastomeric behavior. Figure 3 shows the set strain plotted against elongation for the inventive examples. The inventive PBP-based fabrics exhibit set strains less than about 50 percent strain. For more elastic performance, selection of PBE-based fabrics exhibit the more preferred set strains of less than about 15 percent. In this way, selected inventive examples are shown to have lower set, an aspect of elastomeric behavior. Because the comparative examples hPP examples exhibited elongations to break less than 50 percent strain, they were not able to survive this test.

Another aspect of elastomeric behavior is retractive force. Retained load is a measure of retractive force. Higher retained loads correspond to higher retractive force for a given extension force. Figure 4 shows the MD retained load plotted against elongation. PBP based fabrics are shown to have retained loads of greater than or equal to 0 percent. PBE based fabrics are shown to have retained loads greater than about 15 percent. In applications by themselves or with other components, PBE based fabrics are shown to have greater retractive force. Such behavior translates to greater "holding power" which is

necessary for improved fit and comfort. In many elastic applications, higher holding power is desirable for its greater mechanical ability to fasten one object to another.

The tensile and elastic properties discussed previously are summarized in table 6.

TABLE 6

5

TENSILE AND ELASTIC PROPERTIES FOR INVENTIVE AND COMPARATIVE FABRICS

Example	Normalized Bending Modulus (mN cm) @ 20 gsm avg	Elongation (%) avg	stdev	Normalized Tensile Strength (lb / 1" width) @ 20 gsm avg	stdev	Set Strain (%) avg	stdev	Retained Load 30% strain (%)	uncert
1-1c	1 535	2	0	1 4 1	1 3	n/a	n/a	n/a	-
1-2c	1 408	4	1	1 50	0 5	n/a	n/a	n/a	-
1-3c	0 858	5	2	1 0 8	1 3	n/a	n/a	n/a	-
1-4c	1 069	9	2	1 5 3	2 0	n/a	n/a	n/a	-
1-5c	0 871	9	2	1 7 4	0 0	n/a	n/a	n/a	-
1-6c	0 9 <sub>5</sub> 6	19	11	1 4 0	0 3	n/a	n/a	n/a	-
1-1	0 168	244	188	1.21	1 0	26 0	0 8	0 1	0 2
1-2	0 364	187	5	1 20	0 1	29 1	0 3	0 0	0 0
1-3	0 194	177	35	1 5 1	0 0	25	2	0 4	0 3
1-4	0 364	95	15	1 00	0 1	25 3	0 0	0 0	0 0
1-5	0 228	8	1	1 07	0 0	n/a	-	n/a	-
1-6	0 194	85	11	1 02	0 2	n/a	-	n/a	-
1-7	0 107	141	92	1 13	0 6	n/a	-	n/a	-
1-8	0 228	13	6	1 18	0 2	27 7	-	n/a	-
2-1	n/a	366	106	0 67	0 5	17 9	0 3	9 2	1 1
2-2	0 228	182	38	0 66	0 0	19 2	0 7	5 5	1 0
2-3	0 020	227	28	0 59	0 2	18 8	0 1	6 6	1 1
3-1	0 087	399	149	0 67	0 9	26 5	0 8	n/a	-
3-2	0 107	n/a	n/a		-	n/a	-	n/a	-
3-3	0 068	402	154	0 70	<b>07</b>	8 6	0 8	28 8	1 9
3-4	0 087	481	102	0 81	<b>10</b>	9 1	0 8	28 8	1 6
4-1	0 030	439	89	0 38	0 1	7 5	0 1	35 8	3 2
4-2	0 107	453	159	0 44	0 5	8 1	0 7	32 6	4 4
4-3	n/a	528	159	0 48	0 5	7 6	0 1	35 6	3 5
5-1	0 053	245	16	0 64	0 0	18 0	0 3	8 7	1 6
5-2	0 068	286	49	0 78	0 1	16	1	9 2	2 0
5-3	0 107	154	33	0 64	0 2	17 0	0 2	8 8	0 8
6-1	0 039	141	6	0 63	0 1	15 7	0 1	12 1	1 7
6-2	0 107	165	H	0 64	0 1	16 3	0 2	10 4	1 9
6-3	0 114	185	35	0 72	0 1	16 5	0 3	10 5	0 7
6-4	0 107	167	26	0 64	0 2	15 6	0 5	13 5	1 4
7-1c	n/a	5	1	1 76	0 2	n/a	-	n/a	-
8-1c	n/a	13	2	2 26	0 2	n/a	-	n/a	-
9-1	n/a	17	8	0 91	0 2	n/a	-	n/a	-
2-1c	0 160	7	2	0 18	0 3	n/a	-	n/a	-
2-2c	0 416	14	7	0 63	0 1	n/a	-	n/a	-
2-3c	0 228	12	5	0 53	0 3	n/a	-	n/a	-
2-4c	0 236	23	4	0 52	0 1	n/a	-	n/a	-
3-1c	0 003	56	8	0 16	0 0	7 3	0 4	45	6
3-2c	0 003	n/a	-	0 18	0 1	9 2	0 7	34	12
3-3o	0 003	28	4	0 14	0 1	n/a	-	n/a	-
10-1	n/a	38	5 1	1 0	0 3	23	2	n/a	-

10-2	n/a	238	90	0.41	0.06	n/a	-	11	1
10-3	n/a	94	24	0.39	0.02	7	1	11.4	0.9
10-4	n/a	359	45	0.5 1	0.01	n/a	-	n/a	-
10-5	n/a	121	72	0.8	0.1	13.6	0.7	n/a	-
10-6	n/a	303	142	0.44	0.06	7	1	10	2
10-7	n/a	200	71	0.8	0.2	6.3	0.6	6.7	0.9
10-8	n/a	283	120	0.6	0.1	11	2	39	3
10-9	n/a	53	12	0.7	0.1	13	1	120	40
10-10	n/a	16	1	0.34	0.08	6.3	0.6	12	6
10-11	n/a	90	31	0.5	0.1	5.3	0.6	5.7	0.6

The letter 'O' in the designation denotes a comparative example.

Based on the described discoveries, the following table of preferred ranges for the fibers of this invention is described in Table 7.

5

TABLE 7  
PREFERRED RANGES FOR THE INVENTIVE FABRICS

	Extensible	Elastic
Ethylene (wt.%)	From > 5 to 10	from 10 to 17
Bending Modulus (mN-cm) at < 30 gsm	less than about 0.6	less than about 0.3
Elongation (%)	greater than about 20%	greater than about 350%
Tensile Strength (lbs / 1" width @ 20gsm)	FMD ≥ [-0.00143 × elong(%)+0.823] if elongation is between 20 to 675%	
	FMD ≥ 0.1 lb if elongation is greater than or equal to 675%	
Set Strain (50% hysteresis Test)	less than about 50%	less than about 15%
Retained Load (%) (50% hysteresis Test)	greater than or equal to 0%	greater than about 15%

Selected meltblown fabrics from Table 5 were chosen for fabrication into SMxS laminate structures ('S' denotes spunbond layer, 'M' denotes melt blown layer, and 'x' denotes the number of meltblown layers). They were combined with various 20 gsm spunbond fabrics (Table 8) made with Reicofil 3 technology from Reifenhauer and point bonded at the recommended temperatures for the various materials (hPP, PE and bico) with a calendar roll (21 percent bonding area) to make SMS and SS laminates (Tables 9 and 10).

15

TABLE 8. SPUNBOND NONWOVEN FABRICS

Designation	Composition	Type	Basis Weight (gsm)
12-18	P	hPP	20
12-19	S	hPP	20
12-20	41/59 J/P	propylene-ethylene / hPP blend	20
12-21	Q	polyethylene	20
12-22	R	polyethylene	20
12-23	70/30 P/Q (core/sheath)	hPP /polyethylene (core/sheath)	20

In all cases, inventive laminates made with the meltblown fabrics of example 11-19, had the lowest or equal to the lowest bending modulus. This demonstrates that the low modulus of the meltblown fabrics of the preferred compositional range results in novel laminates. Low modulus translates to softness and better drape in end-use.

5

**TABLE 9. SMxS STRUCTURES AND THEIR BENDING MODULI (N-MM)**

Example	Spunbond Layer	Spunbond Composition	Meltblown Layer			
			Control-	11-18c	11-04c or 11-07c	11-19
13-1c	12-18	P	0.004			
13-2c	12-18	P		0.009		
13-3c	12-18	P			0.008	
13-4	12-18	P				0.006
14-1c	12-19	S	0.003			
14-2c	12-19	S		0.007		
14-3c	12-19	S			0.008	
14-4	12-19	S				0.006
15-1c	12-20	41/59 J/P	0.001			
15-2c	12-20	41/59 J/P		0.003		
15-3c	12-20	41/59 J/P			0.004	
15-4	12-20	41/59 J/P				0.003
16-1c	12-21	Q	0.001			
16-2c	12-21	Q		0.003		
16-3c	12-21	Q			0.003	
16-4	12-21	Q				0.003
17-1c	12-22	R	0.001			
17-2c	12-22	R		0.003		
17-3c	12-22	R			0.004	
17-4	12-22	R				0.003
18-1c	12-23	70/30 P/Q (core/sheath)	0.002			
18-2c	12-23	70/30 P/Q (core/sheath)		0.006		
18-3c	12-23	70/30 P/Q (core/sheath)			0.005	
18-4	12-23	70/30 P/Q (core/sheath)				0.004

The letter 'c' in the designation denotes a comparative example.

Measurement of the peel strength of these laminates by cutting a 5 cm wide strip parallel to the machine direction (MD) and peeling at 100 mm/min in an Instron in a 180° T-peel geometry shows that laminates made with meltblown fabric 11-19 consistently exhibits the highest peel strengths (Figure 6). Peel strength is reported in Newtons per 5 cm width.

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When examined in detail, this result is especially astonishing. First, SMS structures made with meltblown fabric 11-19 exceeded the peel strength of the spunbond fabrics to themselves (the "control" in tables 9 and 10 were two spunbond layers as indicated with no meltblown layer). Second, SMS structures made with meltblown fabric 11-19 exceeded the peel strength of the hPP spunbond fabrics (12-18 and 12-19) to hPP meltblown layers (11-18c, 11-04-c, or 11-07c). Typically, bonds of dissimilar materials are weaker. As a result, the laminates made with meltblown example 11-19 exhibit unexpectedly high bond strengths. Lastly, when at least one spunbond comprises a polyethylene based polymer (12-21,12-22, and 12-23), the peel strength not only exceeds the controls meltblown but also laminates comprising hPP based meltblown (11-18c, 11-04c, or 11-07c). This shows the improved characteristics of the preferred meltblown compositions and also the novel laminates that comprise them.

TABLE 10. SMxS STRUCTURES AND THEIR PEEL STRENGTH (N/5CM WIDTH)

Example	Spunbond	Spunbond Composition	Meltblown			
			control -	11-18c	11-04c or 11-07c	11-19
13-1c	12-18	P	1.6			
13-2c	12-18	P		2.3		
13-3c	12-18	P			2.1	
13-4	12-18	P				5.2
U-1c	12-19	S	2.05			
14-2c	12-19	S		3.1		
14-3c	12-19	S			3.1	
14-4	12-19	S				5
15-1c	12-20	41/59 J/P	0.6			
15-2c	12-20	41/59 J/P		1.25		
15-3c	12-20	41/59 J/P			1.6	
15-4	12-20	41/59 J/P				5.4
16-1c	12-21	Q	1.3			
16-2c	12-21	Q		0		
16-3c	12-21	Q			0	
16-4	12-21	Q				2.6
17-1c	12-22	R	1.9			
17-2c	12-22	R		0		
17-3c	12-22	R			0	
17-4	12-22	R				3.25
18-1c	12-23	70/30 P/Q (core/sheath)	3.5			

18-2c	12-23	70/30 P/Q (core/sheath)	0	
18-3c	12-23	70/30 P/Q (core/sheath)		0
18-4	12-23	70/30 P/Q (core/sheath)		6.3

The letter 'c' in the designation denotes a comparative example.

## WHAT IS CLAIMED IS:

1. A meltblown fabric which has an MD peak tensile force ( $F_{MD}$ ) per one inch width and normalized to 20 gsm basis weight described by the following equations
  - a.  $F_{MD} \geq [-0.00143 \times \text{elong}(\text{percent}) + 0.823]$  if elongation is between 20 to 675 percent
  - b.  $F_{MD} \geq 0.1$  lb if elongation is greater than or equal to 675 percent and wherein the fabric comprises at least one copolymer with at least about 50 weight percent of units derived from propylene and at least about 5 weight percent of units derived from a comonomer other than propylene.
2. The meltblown fabric of claim 1 in which the at least one copolymer is characterized as having  $^{13}\text{C}$  NMR peaks corresponding to a regio-error at about 14.6 and about 15.7 ppm, the peaks being of about equal intensity.
3. The meltblown fabric of Claim 1 wherein the comonomer comprises 3 to 20 wt. percent ethylene.
4. The meltblown fabric of Claim 1 wherein the comonomer comprises 9 to 20 wt. percent ethylene.
5. The meltblown fabric of Claim 1 wherein the copolymer has a MFR from 25 to 5000.
6. The meltblown fabric of Claim 1 wherein the copolymer has undergone chemically induced chain scission and has a MFR from 50 to 5000.
7. The meltblown fabric of Claim 6 wherein the chain scission is caused by combining the composition with a free radical initiator prior to extrusion.
8. The meltblown fabric of Claim 7 wherein the free radical initiator is a peroxide type.
9. The meltblown fabric of Claim 7 wherein the rheology modifier is a non-peroxide type.
10. The meltblown fabric of Claim 9 wherein the non-peroxide type rheology modifier is a hydroxyl amine ester.
11. The meltblown fabric of Claim 6 wherein the chain scission is caused by combining the composition with at least one peroxide type and one non-peroxide type of free radical initiators.
12. The meltblown fabric of Claim 1 in which the average fiber diameter is less than 10 microns.
13. The meltblown fabric of Claim 1 which has immediate set of less than or equal to about 50 percent as measured by a 50 percent 1 cycle test.

14. The meltblown fabric of Claim 1 which has retained load greater than or equal to about 0 percent as measured by a 75 percent 1 cycle test.
15. The meltblown fabric of Claim 1 which has retained load greater than or equal to about 15 percent as measured by a 75 percent 1 cycle test.
- 5 16. The meltblown fabric of Claim 1 wherein the fabric comprises less than about 10 percent by weight hPP and/or RCP.
17. The meltblown fabric of Claim 1 wherein the fabric comprises less than about 8 percent by weight hPP and/or RCP.
18. The meltblown fabric of Claim 1 wherein the fabric comprises less than about 6 percent  
10 by weight hPP and/or RCP.
19. The meltblown fabric of Claim 1 wherein the fabric comprises less than about 4 percent by weight hPP and/or RCP.
20. A nonwoven laminate comprising the meltblown nonwoven layer of any one of Claims 1-19 and at least one spunbond nonwoven layer.
- 15 21. The nonwoven laminate of Claim 20 wherein the spunbond layer comprises fibers characterized in that a polyethylene based material comprises at least a portion of the surface of the fiber.
22. The nonwoven laminate of Claim 20 wherein the spunbond layer comprises a bicomponent fiber.
- 20 23. The nonwoven laminate of claim 22 wherein the bicomponent fiber is in a sheath-core configuration.
24. The nonwoven laminate of Claim 23 wherein the spunbond layer comprises a monofilament fiber.
- 25 25. The nonwoven laminate of Claim 24 wherein the spunbond layer comprises a polyolefin other than polyethylene.
26. A nonwoven laminate structure comprising at least two nonwoven layers, said nonwoven laminate structure being characterized by having an overall bending modulus according to ASTM D 5732-95 of 0.005 Nmm or less and a peel strength between the nonwoven layers of more than 2 N/5cm; wherein at least one of the nonwoven layers  
30 comprises fiber comprising at least one polymer with at least about 50 weight percent of units derived from propylene.

27. The nonwoven laminate structure of Claim 26 further characterized by having hydrohead behavior greater than about 200 mm H<sub>2</sub>O normalized to a basis weight of 25 gsm.
28. The nonwoven laminate structure of Claim 26 wherein the at least two nonwoven layers include at least one meltblown layer and at least one spunbond layer
29. The nonwoven laminate structure of claim 28 further comprising at least one additional meltblown or spunbond layer.
30. The nonwoven laminate structure of claim 26 wherein at least one nonwoven layer is a meltblown nonwoven layer which comprises meltblown fibers comprising a propylene based polymer characterized by having one or more of the following traits:
- less than 50 percent crystallinity
  - flex modulus less than 50 kpsi
  - melting point less than about 140° C; and/or heat of fusion less than 80 J/g
31. The nonwoven laminate structure of claim 30 wherein the meltblown fibers are further characterized as comprising copolymers of propylene and an alpha-olefin, wherein the alpha olefin is preferably ethylene.
32. The meltblown nonwoven layer of claim 31 wherein the alpha olefin is ethylene.
33. The nonwoven laminate structure of claim 30 in which the propylene based polymer is further characterized as having <sup>13</sup>C NMR peaks corresponding to a regio-error at about 14.6 and about 15.7 ppm, the peaks being of about equal intensity.
34. The nonwoven laminate structure of Claim 30 wherein the propylene based polymer comprises 3 to 20 wt. percent ethylene.
35. The nonwoven laminate structure of Claim 30 wherein the propylene based polymer comprises 9 to 20 wt. percent ethylene.
36. The nonwoven laminate structure of Claim 30 wherein the propylene based polymer has an MFR from 25 to 5000.
37. The nonwoven laminate structure of Claim 30 wherein the propylene based polymer has undergone chemically induced chain scission and has an MFR from 50 to 5000.
38. The nonwoven laminate structure of Claim 37 wherein the chain scission is caused by combining the composition with a free radical initiator prior to extrusion.
39. The nonwoven laminate structure of Claim 38 wherein the free radical initiator is a peroxide type.

40. The nonwoven laminate structure of Claim 38 wherein the free radical initiator is a non-  
peroxide type.
41. The nonwoven laminate structure of Claim 37 wherein the chain scission is caused by  
combining the composition with at least one peroxide type and one non-peroxide type of  
5 free radical initiators.
42. The nonwoven laminate structure of Claim 30 in which the average fiber diameter of the  
meltblown fibers is less than about 12 microns.
43. The nonwoven laminate structure of Claim 28 in which the spunbond layer comprises  
fibers characterized as having polyethylene based material comprising at least a portion  
10 of the surface of the fiber.
44. The spunbond layer of Claim 26 comprising fibers of a bicomponent structure.
45. The spunbond layer of Claim 44 in which the bicomponent fibers have a sheath-core  
configuration.
46. A nonwoven laminate comprising at least one meltblown nonwoven layer and at least  
15 one spunbond layer wherein:  
the at least one melt blown layer comprises fibers comprising polymer having at least  
about 50 weight percent of units derived from propylene; and  
the at least one spunbond nonwoven layer comprises fibers characterized in that a  
polyethylene based material comprises at least a portion of the surface of the fiber.
- 20 47. The nonwoven laminat of Claim 46 wherein the at least one meltblown layer comprises  
fibers comprising polymer having at least about 50 weight percent of units derived from  
propylene and at least about 5 weight percent of units derived from a monomer other  
than propylene.

FIG. 1

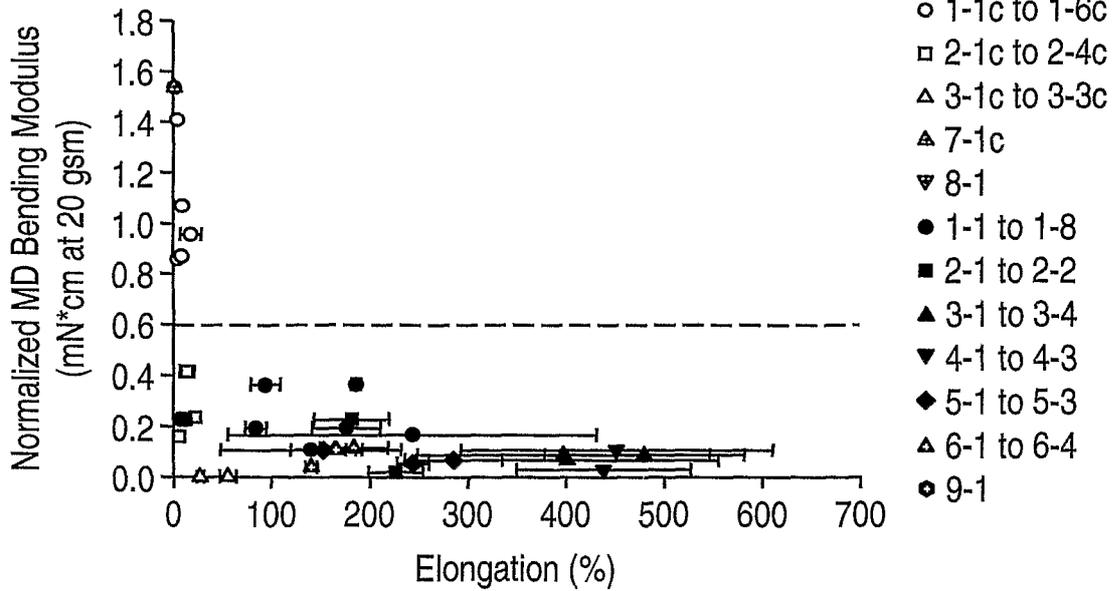


FIG. 2

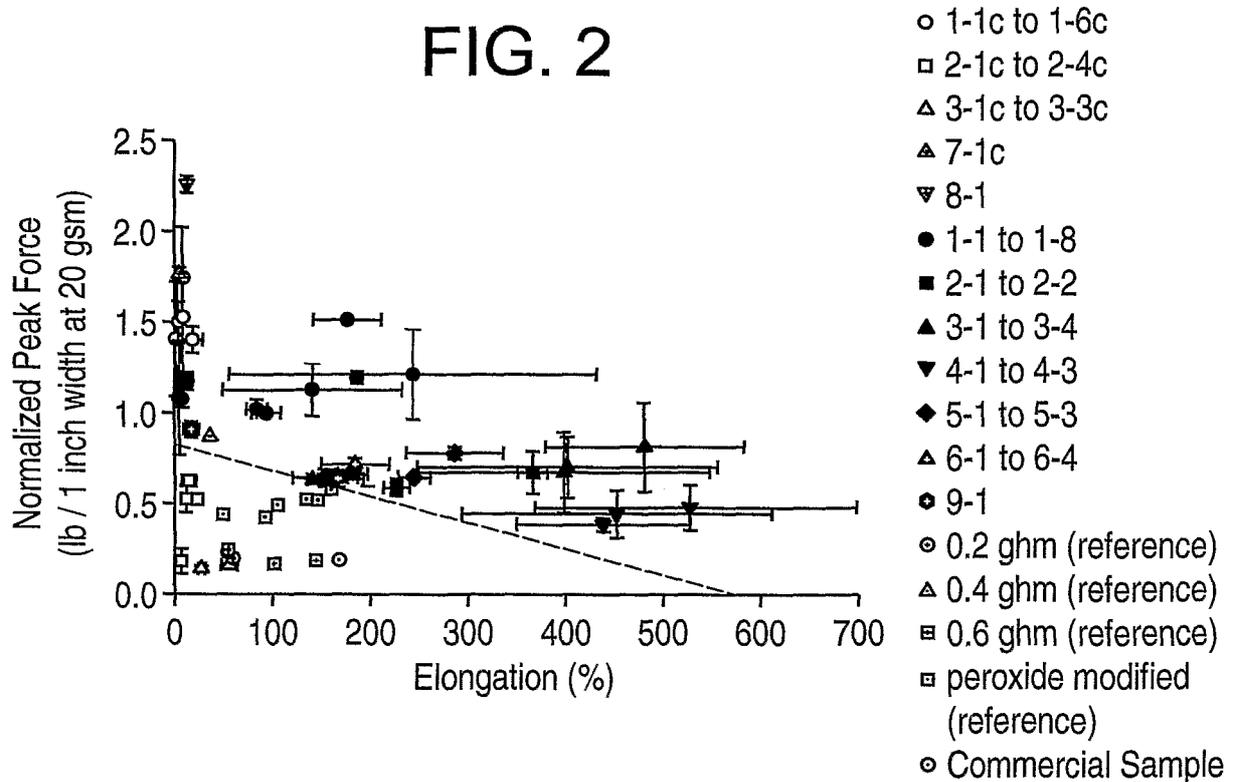


FIG. 3

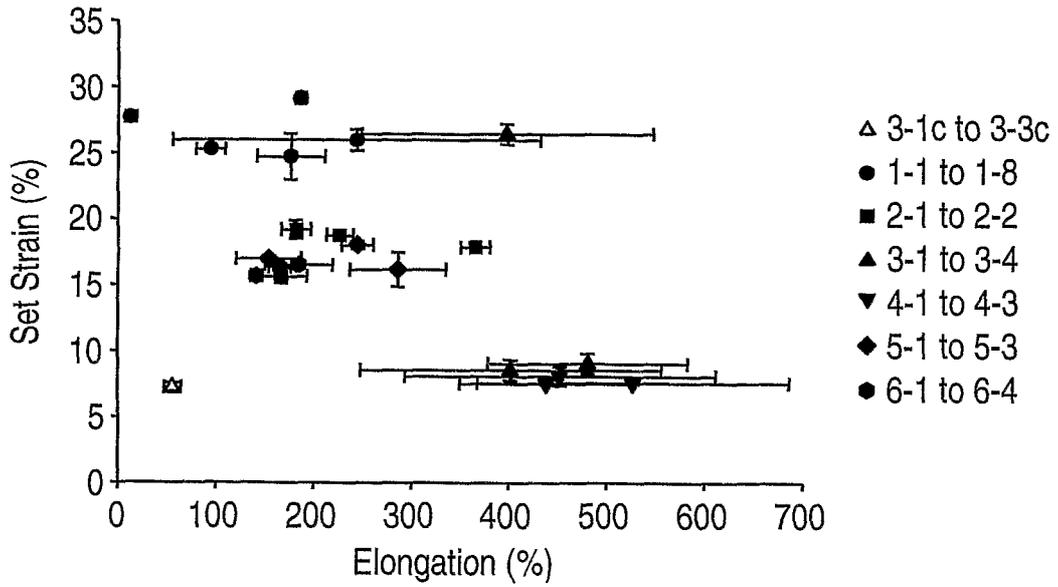


FIG. 4

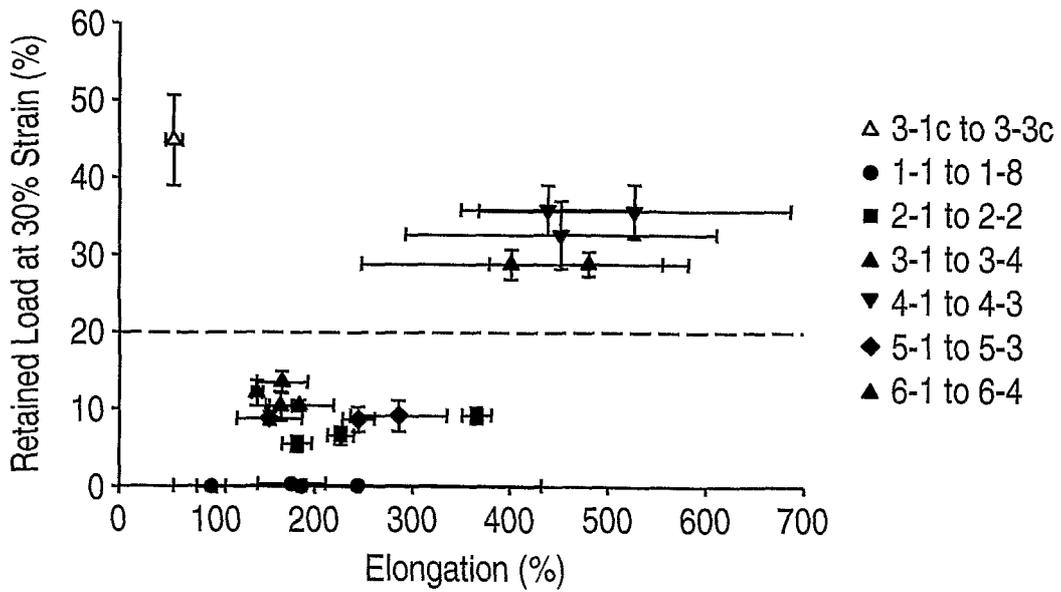


FIG. 5

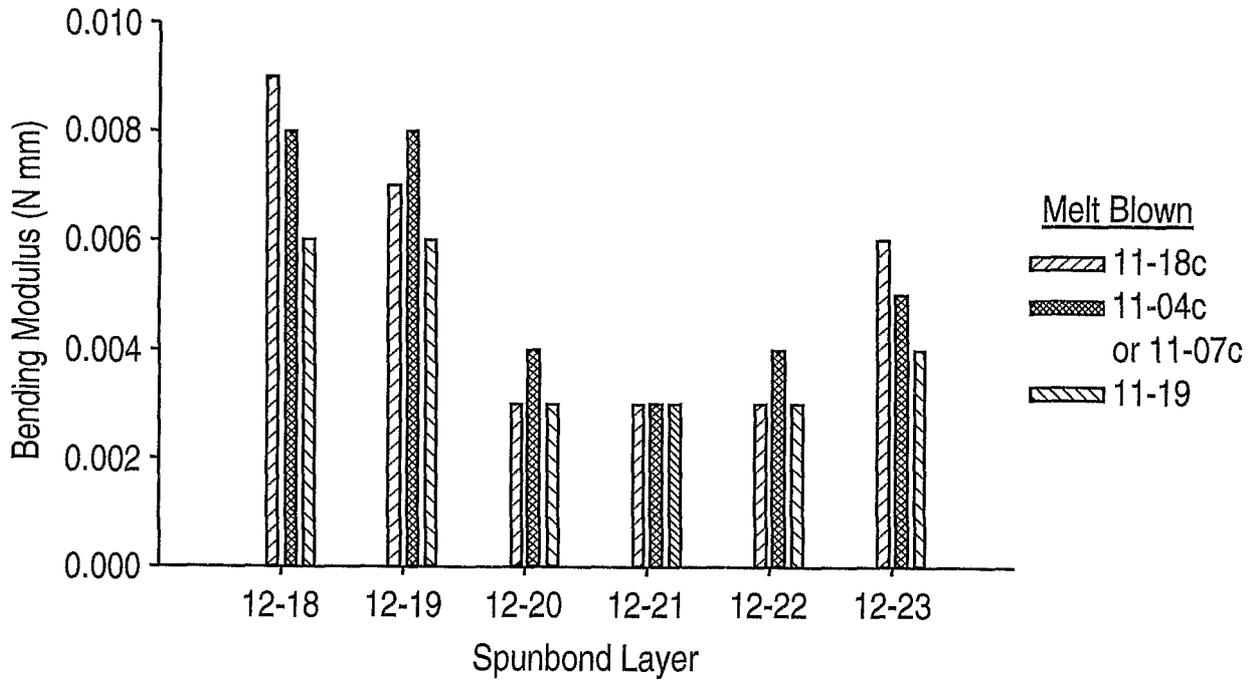
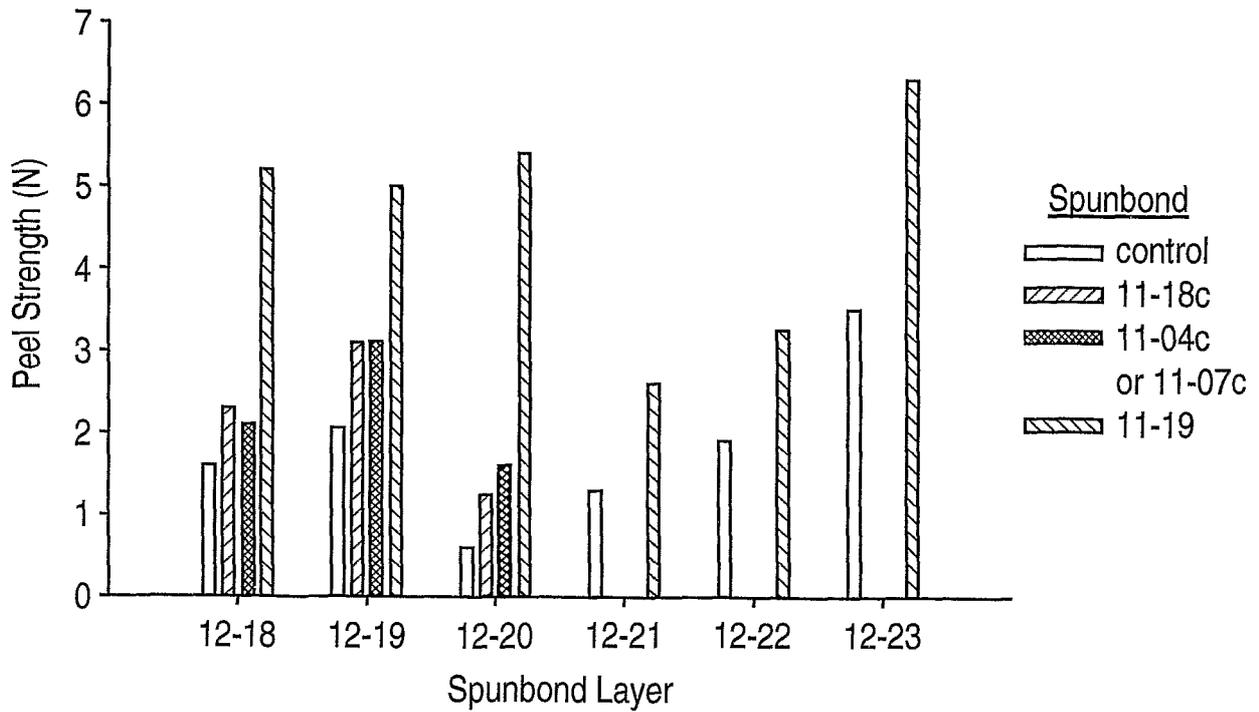


FIG. 6



## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2006/030416

## A. CLASSIFICATION OF SUBJECT MATTER

INV. D04H1/42 D04H13/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
D04H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal , WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	JP 2003 138075 A (JAPAN POLYCHEM CORP) 14 May 2003 (2003-05-14) abstract paragraphs [0006] - [0016], [0047], [0057]	1,3,5-8
X	WO 99/10580 A (KIMBERLY CLARK CO [US]) 4 March 1999 (1999-03-04)  page 3, line 12 - page 5, line 22; figure 1  -/-	1,3-5, 12,20, 21,26, 28-32, 34-37, 42,43, 46,47

 Further documents are listed in the continuation of Box C See patent family annex

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"&amp;" document member of the same patent family

Date of the actual completion of the international search

10 November 2006

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/030416

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International application No

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