(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 621 091 B9

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see
Description Paragraph(s) 36, 39, 41
Claims EN 1

(48) Corrigendum issued on:
02.09.2015 Bulletin 2015/36

(45) Date of publication and mention of the grant of the patent:
19.01.2011 Bulletin 2011/03

(21) Application number: **05014085.4**

(22) Date of filing: **29.06.2005**

(51) Int Cl.:
A43B 13/42 *(2006.01)* ***B32B 27/36*** *(2006.01)*
B29C 47/00 *(2006.01)* ***C09J 167/04*** *(2006.01)*

(54) **Stiffeners for use in footwear**

Schuhversteifungselemente

Éléments pour renforcer des chaussures

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR

(30) Priority: **01.07.2004 US 584519 P**
30.12.2004 US 640947 P

(43) Date of publication of application:
01.02.2006 Bulletin 2006/05

(73) Proprietor: **Stanbee Company, Inc.**
Carlstadt NJ 07072 (US)

(72) Inventor: **Goldberg, Bruce**
Clifton
New Jersey 07012 (US)

(74) Representative: **Müller-Boré & Partner Patentanwälte PartG mbB**
Friedenheimer Brücke 21
80639 München (DE)

(56) References cited:

EP-A- 0 364 301 **WO-A-00/30485**
WO-A-00/41585 **WO-A-01/72162**
WO-A-97/38060 **WO-A-03/066329**
FR-A- 2 623 980 **GB-A- 2 291 880**
US-A- 5 532 066

- **PATENT ABSTRACTS OF JAPAN vol. 2003, no. 12, 5 December 2003 (2003-12-05) & JP 2004 351634 A (KIRA SHIKO:KK), 16 December 2004 (2004-12-16)**
- **PATENT ABSTRACTS OF JAPAN vol. 015, no. 436 (C-0882), 7 November 1991 (1991-11-07) & JP 03 185051 A (UNITIKA LTD), 13 August 1991 (1991-08-13)**
- **DATABASE WPI Section Ch, Week 200211 Derwent Publications Ltd., London, GB; Class A92, AN 2002-075910 XP002342889 & CN 1 312 165 A (BILI PACKAGE MATERIAL CO LTD PINGHU) 12 September 2001 (2001-09-12)**

EP 1 621 091 B9

Description

[0001] The invention relates to stiffeners, such as the stiffeners used in the manufacture of shoes to retain the shape of heel and toe portions of the footwear.

[0002] There are a number of different types of stiffeners used in the shoe industry. United States Patent Nos. 3,523,103; 3,590,411; 3,647,616; 3,891,785; 3,973,285; 4,814,037; 6,391,380 and 6,475,619 disclose methods and materials for improving the stiffness and adhesive qualities of materials for use in the footwear industry (all of which are incorporated by referenced). The stiffening plastic resins are selected from styrene butadiene, polystyrene, polyvinylacetate, acrylic as well as other polymer lattices that may be saturated into a needle punch non woven fabric. Some of these types of stiffeners have hot melt adhesives coated onto their surfaces and are heat activated to bond to the shoe upper and lining. Some are activated with solvents and do not have heat activated hot melt adhesives. A second group of stiffeners are premolded materials made from polyvinylchloride, ionomers or thermoplastic rubbers (TPR). These premolded stiffeners require an adhesive to be painted on the surface for bonding to the shoe components. There are stiffeners that are made via extrusion of a resin such as an ionomer or other thermoplastic polymers and then require an extrusion coating of an adhesive onto the polymer sheet. The last category comprises stiffeners that are made from powders that are admixtures of a filler or hard material with an adhesive or softer material. These polymer powder blends are then heat sintered to produce a stiffener.

[0003] WO 03/066329 A1 describes polyester or copolyester/polyolefin laminate structures and methods of making the same. WO 01/72162 A1 describes improvement in co-extruded thermoplastic structural material for footwear. GB-A-2 291 880 describes a material suitable for use as a shoe stiffener. WO 00/30485 describes coextruded thermoplastic structural material for shoes and manufacturing procedure of coextruded material. FR 2 623 980 describes reinforcement material for shoes. US-patent 5,532,066 describes a laminate of ethylene-alkyl acrylate copolymer and polyester. EP-A-0 364 301 describes nonoriented polyester films with modified heat seal layer.

[0004] The ideal characteristic of the stiffener is to have high resiliency and good stiffness for a given weight of material. The saturated stiffeners can be made stiff but usually the stiffer grades do not have high resiliency. The saturated stiffeners, the premolded stiffeners and the extruded stiffeners all require an extra processing step to have an adhesive applied to the surface. The powder coated stiffeners usually involve a need for cryogrinding to be able to create a fine powder from a low melting point adhesive which results in added costs as well as a need for a critical particle size distribution. The powder coated materials, since they are sintered, are also less tough or strong and need extra weight for a given level of stiffness since the sintering action does not form a true melt of the material to maximize the physical properties. These materials also need high levels of the adhesive component in order to get good bonding to the various substrates that they will be attached to. This adds additional cost and additional weight. When hot melting the saturated materials or the extruded materials they need a significant amount of hot melt adhesive to be coated onto their surfaces in a separate step.

[0005] There are processes and products that are used in the packaging industry where a tie layer of adhesive is added to another resin to produce a very thin layer to bond these various layers together. Usually this is done with adhesive tie layers in which the adhesive component is similar in melt viscosity and melting point to the other layers. The process to produce these materials is an extrusion process that uses multiple extruders and either a multicomponent die block or a manifold die.

[0006] The present invention overcomes a number of the deficiencies listed above. The present invention as defined in claim 1 uses a combination of a stiffening plastic resin comprising polymers of polyethylene terephthalate glycol (PETG) copolyester and low melting point plastic adhesive resins comprising polycaprolactone, to form a polymer sheet stiffener that has both stiffening properties and adhesive properties in one step. The polymers of PETG copolyester and polycaprolactone are combined in an "ABA" manner to obtain the desired stiffening and adhesive properties.

[0007] Additional stiffening plastic resins are known in the art, examples are styrene resins, styrene-butadiene resins, vinyl acetate resins, vinyl chloride resins, acrylic resins, extruded thermoplastic or powder coated thermoplastic materials which may be selected from the group consisting of polyvinyl chloride, ionomers, high, medium or low density polyethylene, polypropylene, polyesters, polystyrene and copolymers and compatible blends of such polymers. Examples of commercially available stiffeners are PETG, PET and copolyesters, such as, but not limited to, GP001 polyester, all of which are available from Eastman Chemicals.

[0008] GP001 is a copolyester with a vicat softening temperature of 74°C and a glass transition temperature of 75°C. At a thickness of 0.2540 mm (10 mils), a film of GP001 copolyester exhibited a density of 1.30g/m^3, an Elmendorf tear resistance of 7.5 N (M.D. and T.D.), a PPT tear resistance of 61 (M.D.) and 66N (T.D.), a tensile strength at break of 53 Mpa (7600 psi at M.D. and T.D.), a tensile modulus of (M.D.) 1570 Mpa (2.3×10^5 psi) and (T.D.) 1560 Mpa (2.3×10^5 psi), a dart impact at 23°C of 355g, an elongation at break of 5% (M.D. and T.D.), a Tear Propagation Resistance, Split Tear Method (at 254 mm/min) (M.D. and T.D.) of 15.7N. The GP001 Mechanical properties for injection molding are as follows, tensile stress at break of 22 Mpa (3200 psi), tensile stress at yield of 51 MPa (7400 psi), and elongation at break of 184%, a tensile modulus of 2275 Mpa (3.3×10^5 psi), a flexural yield strength of 73 Mpa (10600 psi).

[0009] Polycaprolactone has good water, oil, solvent and chlorine resistance. It has a low melting-point (58-60°C) and low viscosity, and it is easy to process. Additional low melting point plastic adhesive resins, such as plastic resins with a melting point below 85°C can also be employed in the present invention. An additional low melting point plastic adhesive resin is ethylene methyl acrylate copolymer, sold commercially as 2260 EMAC by Eastman Chemicals. 2260 EMAC has a melting point of 76°C.

[0010] EMAC 2260 is ethylene methyl acrylate copolymer with a melt index of 2.1g/10 min., a density of 944 kg/m^3, a vicat softening temperature of 50°C, a brittleness temperature of < -73°C, a durometer hardness (Shore D Scale) of 37, a methyl acrylate content of 24%, a tensile stress at break (500 mm/min) of 11Mpa, and an elongation at break (500 mm/min) of 835%, and a melting point of 76-77°C.

[0011] The stiffener may be evaluated to determine the adhesive bonding strength of the finished product by die cutting a piece of the stiffener to be tested and inserting the stiffener between two pieces of a non-woven lining material that is a 35% poly ester blend having a thickness of 0.07 cm (0.029 inches). The three pieces are held together and placed into a back part heel counter molding machine with the female mold at 82.2°C (180°F) and the male mold at 143.3°C (290°F). The mold is closed and held in position for 17 seconds. The mold is opened and the laminate is placed, at room temperature, in a laminate cooling station having the desired shape of the final product. The shaped heel counter is now rigid and the stiffener is bonded to the two pieces of non-woven lining material. The adhesive test requires that the three part laminate remain bonded together when manual pressure is applied to pull the components apart. This determines if the stiffening material has good adhesive qualities. The resiliency test is based on making a thumb indent on the side of the heel counter and evaluating the degree with which the indent bounces back. An acceptable bounce is when the indent bounces back immediately with a "ping-pong" sound. This determines if the stiffening material is resilient.

[0012] One process involves co-extruding with either a coextrusion block or a manifold die using polymers of PETG copolyester with adhesives comprising polycaprolactone, to form a polymer sheet stiffener that has both stiffening properties and adhesive properties in one step. The uniqueness of the process and the material is that it allows for two materials of significantly different melting points and viscosity to form a sheet material in one step. These sheets can then be heat activated to form a bond with the shoe components when heated and molded and at the same time produce a stiff material depending on the ratio of the ingredients and their weight. The formulation produces a stiff material with high resiliency and toughness. The two unique characteristics of this product and process are the fact that they can coextrude and form an acceptable sheet from two highly different melt index and melting point materials. Additionally it is more cost effective to perform in one step what usually takes two steps and at the same time it is possible to use a smaller amount of the adhesive resin since it all sits on the two outer surfaces of the sheet. It is also possible to use regrind in place of virgin polymer.

[0013] The copolyester of the coextruded stiffener preferably is the Eastman Chemical Eastar 6763, which has a softening point of 85°C (185°F) and is usually extruded into a film at extrusion temperatures of 246-274°C (475-525°F). The adhesive preferably is a polycaprolactone and most preferably Dow Chemical Tone 767 (Tone) which has a melting point of 60°C (140°F) and a melt flow of 1.9 or Tone 787 with a melt index of 0.5. The melt index is determined via ASTM D1238-73, which is run at 80°C and at 0.3 Mpa (44 psi) and measured in g/10 min. The PETG has a flex modulus of 2068 Mpa (300,000 psi) and the Tone has a flex modulus of 434 Mpa (63,000 psi). Therefore, the PETG is the component that adds stiffness to the material and varying its level will vary the level of stiffness. The Tone normally extrudes at 93-120°C (200-250°F). The uniqueness of the process and the product is the fact that these two materials are brought together in the die and they maintain their integral integrity. The Tone remains on the outer surfaces as an adhesive and the PETG forms the internal core to add the stiffness quality.

[0014] While the two materials listed above are illustrated one is not limited to these materials and one could coextrude PET polyester as the core or iononmer and use the above adhesive, ethylene vinyl acetate adhesives, ethylene meth-acrylate adhesives or copolyesters.

[0015] The below examples resulted in several novel discoveries. The manifold die works well forming an "ABA" structure wherein the adhesive is on both sides of the polymer stiffener. The PETG regrind does not need to be dried under environmental conditions 23.9°C (75°F) and less than 50% humidity. The Tone can run at higher temperatures without too much reduction in viscosity and still results in a good coating. The casting rolls can be run at a temperature of about 12.8°C (55°F). The use of higher temperatures at the die, the Tone feed pipes and the extruder reduces and/or eliminates the potential of score die lines. These lines come from the adhesive coating and not from the stiffener polymer. The use of a flex lip die and the 100 mesh screen pack help in giving a better surface and minimize contamination. A cast roll works well, but these rolls do not allow for gauge control. The gauge control occurs from the extruder speed and the die opening. There is a limitation on how much turn down one can get with a single die lip, and die modifications can be made to increase the turn down. Good bonds occurred with the Tone coating and the Tone coating stayed on the polymer surfaces even at higher temperatures. Good bonds occurred with the 90/10 PETG/Tone ratio even at lower weights where the Tone layers were less than 50g/m^2. PET regrind that is dried will also work on in the present invention with the Tone even though it has to be extruded at much higher extrusion temperatures and higher die temperatures. The polyethylene terephthalate (PET) required at least 287.8°C (550°F) for the PET extruder, which then resulted in good Tone flow and good bonding.

[0016] The following examples illustrate the process and the materials produced. The units "# / hr" and "# hr" mean x 0.45 kg "(pounds) / hr" and x 0.45 kg "(pounds) hr", respectively.

[0017] Examples 1-9 related to the process of mixing the polymer stiffener and the adhesive material to produce a polymer sheet stiffener in a single mixing and/or extruding step. Examples 1-9 are for reference.

EXAMPLE 1

[0018] The copolyester is a PETG copolyester, specifically Eastman Chemical Eastar 6763 and the adhesive is a polycaprolactone, specifically Tone 767. The materials have significantly different properties that can be made homogeneous by processing them through a READCO continuous mixer (READCO Company, York, PA.) at temperatures in the range of 193.3-204.4°C (380-400°F). This equipment does not require a powder form of the material and allows for the dissimilar materials to form a homogeneous melt that will produce a tough, stiff and adhesive activated sheet of material. 40 parts of Tone 767 and 60 parts of PETG copolyester were fed separately into a READCO 5.08 cm (2 inch) continuous mixer with the temperatures set at 190.6°C (375°F) and the slot die at 218.3°C (425°F). The feed rate was 27 kg (60 lbs)/hr at a screw speed of 150 rpm. The resulting sheet was passed through a set of cooling rolls to produce a sheet with a thickness of 1.0160-1.0922 mm (40-43 mils).

EXAMPLE 2

[0019] This example had the same conditions as Example 1 except 50 parts of Tone and 50 parts of PETG were fed into the mixer to produce the same thickness sheet.

EXAMPLE 3

[0020] This example had the same conditions as Example 1 except that 60 parts of Tone and 40 Parts of PETG were used to produce a sheet in the range of 1.0160 - 1.0922 mm (40-43 mils).

EXAMPLE 4

[0021] This example had the same conditions as Example 1 except 60 parts of Tone and 40 parts of PETG were used to produce a sheet of approximately 1.5240 mm (60 mils) in thickness.

EXAMPLE 5

[0022] This example had the same conditions as Example 1 except that 50 parts of Tone and 50 parts of PETG were used to produce a sheet that was 1.5240 mm (60 mils) thick.

EXAMPLE 6

[0023] This example had the same conditions as Example 1 except that 40 parts of Tone and 60 parts of PETG were used to produce a sheet that was 1.5240 mm (60 mils) thick.

EXAMPLE 7

[0024] This example had the same conditions as Example 1 except that 40 parts of Tone and 60 Parts of PETG were used to produce a sheet that was 2.0320 mm (80 mils) thick.

EXAMPLE 8

[0025] This example had the same conditions as Example 1 except that 50 parts of Tone and 50 parts of PETG were used to produce a sheet that was 2.0320 mm (80 mils) thick.

EXAMPLE 9

[0026] This example had the same conditions as Example 1 except that 60 parts of Tone and 40 parts of PETG were used to produce a sheet that was 1.7780 - 1.9050 mm (70-75 mils) thick.

[0027] The materials produced from Examples 1-9 were tested for stiffness and resiliency using the Satra test procedures # TM 83. This test is a standard that is used in the footwear industry. The results are shown in Table I below:

TABLE I - STIFFNESS AND RESILIENCY

Example No:	1	2	3	4	5	6	7	8	9
Wt. (g/m^2)	1293	1344	1317	1627	1741	1867	2511	2496	2236
Thickness (mm)	1.0160-1.0668	1.0414-1.1684	1.0668-1.0922	1.3208-1.4478	1.3716-1.4478	1.5240-1.5748	2.0320-2.1082	2.0320-2.1336	1.8542-1.9050
(Thickness (mils)	40-42	41-46	42-43	52-57	54-57	60-62	80-83	80-84	73-75)
1st Collapse (kg)	17	16.5	11.4	19.7	26.4	37.1	63.2	51.8	43
10th Collapse (kg)	12.4	9.6	7.7	14.2	16.6	24.5	40.4	38.6	28.9
% Resiliency	73	58	68	72	63	66	64	75	67

[0028] Examples 10-25 relate to the process of co-extruding the polymer stiffener and the adhesive material to produce a polymer sheet stiffener in a single extruding step. Examples 19-23 are for reference.

EXAMPLE 10

[0029] Two WELEX extruders are used in this example along with a WELEX coextrusion block. A sheet die with a maximum gap of 1.0160 mm (40 mils) was used. A 5.71 cm (2-¼ inch) WELEX extruder is used to extrude the PETG core material with a temperature profile of 162.8°C, 176.7°C, 190°C and 204.4°C (325°F, 350°F, 375°F and 400°F). The die temperature was maintained between 198.9-210°C (390-410°F). A temperature profile of 162.8°C, 190.6°C, 210°C and 215.6°C (325°F, 375°F, 410°F and 420°F) was also evaluated. PETG in the form of regrind chips was used as the feed to the extruder. The second extruder was a 2.54 cm (1-inch) WELEX extruder that employed Tone pellets. This second extruder was maintained at a temperature profile of 73.9°C, 110°C and 123.9°C (165°F, 230°F and 255°F). The PETG was fed into the center of the coextrusion die block and the Tone into the two outer areas. The profile produced was a sheet of 0.8382 mm (33 mils) in thickness that was extruded onto a set of 3 cooling rolls and wound up. The extrusion rate of the PETG was kept constant at 32.4 kg (72) #/hr and the extrusion rate of the Tone was varied to give products that had ratios of PETG/Tone of 70/30, 80/20 and 90/10. The 70/30 ratio resulted from an extrusion speed of 32.4 kg (72 #)/hr of PETG and 13.5 kg (30 #)hr of the Tone, whereas the 90/10 ratio had an extrusion speed of 32.4 kg (72 #/)/hr of PETG and 3.51 kg (7.8 #)/hr of Tone. The Tone formed on both sides of the PETG. Samples of the sheets were placed on a melting point bar apparatus that had varying temperatures and the surface tack of the pieces was measured by feeling them at various temperatures. All samples tested at 60-100°C (140-212°F) yielded good tack, which meant that the Tone was on the surface, If The Tone was not there then at these temperatures there would be no tack. Samples of the sheets were taken and placed between a piece of leather and lining material, which was then placed in a mold where the bondline temperature was 70°C (150°F), and the materials were compressed. The PETG/Tone material formed an excellent bond to the leather and the lining.

[0030] Surprisingly the lower melting point resin did not dissolve in the higher melting point resin and the adhesive still maintained its integrity to form a separate coating on the PETG.

[0031] A sample sheet of 0.7874-0.8382 mm (31-33 mils) was cut into a circle and molded to form a dome looking piece to be tested via the Satra dome testing measurement to determine stiffness and resiliency. Table II reproduces the obtained data:

TABLE II - STIFFNESS AND RESILIENCY EXAMPLE 10

Wt. (g/m^2)	1035
Thickness (mm)	0.7874-0.8382
(Thickness (mils)	31-33)
1 st Collapse (kg)	15.3
10th Collapse (kg)	14.5
% Resiliency	95

EXAMPLE 11

[0032] Three extruders were used in this experiment. Two were Crompton Davis Standard 3.17 cm (1-¼ inch) extruders and one was a 6.35 cm (2-½ inch) extruder. The larger extruder fed the PETG at a constant rate and the two smaller extruders fed the Tone. The materials were fed into a sheet manifold die where the center received the PETG melt and the two outer layers received the Tone.

[0033] The equipment used was as follows:

Extruders: One 6.35 cm (2½-inch) Davis Standard extruder with a 30/l UD single stage barrier screw. Five zone heat and cooling. Two 3.17 cm (1¼-inch) Davis Standard extruders with a 24/1 UD barrier single stage screw. All extruders did not have gear pumps or static mixers on them. A gravimetric feeder was above the (6.35 cm (2½-inch) extruder. The two 3.17 cm (1¼-inch) extruders fed to the side of the die and the 6.35 cm (2½-inch) fed to the center of the die. All extruders had throat cooling and throat cooled to 10°C (50°F);

Die: Three layer manifold flexible lip die with separate heating on outer manifolds and center as well as lip. The die was an EDI 30.48 cm (12 inch) wide unit with a coextrusion block for ABA coextrusion. Screen changers on all machines with 20/100/20 mesh packs;

Rolls: Two casting rolls parallel to each other in horizontal plain of 76.2 cm (30-inch) face with cooling on both rolls;
Thickness monitor: Beta type gauge;
Wind-up station;
Cutting table with paper cutter to cut sheet;
Chiller: for rolls and extruders.

[0034] (Note: thickness controlled by die lips and not rolls. Wind up used during start up and each thickness change until reach equilibrium and then bypassed wind up to go to cutting table to cut sheets about 91.44 cm (3 feet long).)

[0035] The PETG was not dried and was fed into the 6.35 cm (2½-inch) extruder. The Tone was not dried and was fed into the feed hopper feed to each of the 3.17 cm (1¼-inch) extruders at PETG Regrind - 6.35 (2½)-extruder - start-up at 10 rpm. The extruder was maintained at a temperature of 162.8°C, 190.6°C, 204.4°C, 210°C and 215°C (325°F, 375°F, 400°F, 410°F and 420°F). The screen changer, clamps and other piping were maintained at 210°C (410°F). The output was 20.7 kg (46 #)/hr. The feed throat was maintained at 10°C (50°F). The die was maintained at 204.4°C (400°F). The die lip heater was maintained at 100% and also used an air knife. There were no noticeable lines in the extrudate or the sheet of PETG.

[0036] The Tone extruders were set at 65.6°C, 110°C and 121.1°C (150°F, 230°F and 250°F) and the die at 121.1°C (250°F). The co-extruders were set at 18/11/11 rpms (PETG/Tone A/Tone C) to produce 69.3 kg (154#)/hr. The rolls temperature was set at 7.2°C (45°F). The die gap was set at 1.2700 mm (50 mils). The Roll temperature was then raised to 12.8°C (55°F). This produced sheet with a width of 26.67 cm (10½ inches) wherein the Tone coated section was about 19.05 cm (7½ inches) wide. The pressure in PETG extruder was 14 Mpa (2065 psi), the pressure in the Tone A extruder was 4 Mpa (574 psi) and the pressure in the Tone C extruder was 2.7 Mpa (387 psi). Roll speed was set at 7.5 fpm. The Melt temperature was set at 202.8°C (397F). The air knife was placed at the exit of die and helped to cool the sheet before they were transferred to the rolls. This process produced sheet with a thickness of 1.3462-1.3970 mm (53-55 mils) and a weight of about 1700 g/m^2, sheets with a thickness of 1.2954-1.4224 mm (51-56 mils) and a weight of 1611 g/m^2, and sheets with a thickness of 1.1430-1.2192 mm (45-48 mils) and a weight of about 1500 g/m^2. All three materials were tested on a melting point bar and produced good tack at 70-90°C (158-194°F).

[0037] There was a pressure difference between the two Tone extruders because of the longer run of pipe to the die.

[0038] The following examples illustrate the various formulations evaluated and the test results obtained on the finished sheets produced.

EXAMPLE 12

[0039] This example was prepared in accordance with Example 11, however, the extrusion rates were reduced to 16/10/10 rpm to produce sheets with a thickness of 1.0160 mm (40 mils) and a weight of about 1300 g/m^2. Extrusion pressure was 13 Mpa (1896 psi) for the PETG and 3.7 Mpa (539 psi) and 2.4 Mpa (341 psi) for the Tone A and Tone C extruders respectively. The temperature in all the melt pipes was set at 204.4°C (400°F), the die temperature was set at 204.4°C (400°F) and roll speeds were set at 7.5 fpm. This resulted in sheets with a thickness of 27.94 cm (11 inches). Circles of sheet had thickness of 1.0668-1.1430 mm (42-45 mils) and a weight of 1306 g/m^2 and a thickness of 1.0160 mm (40 mils) and a weight of 1273 g/m^2.

EXAMPLE 13

[0040] This example was prepared in accordance with Example 12, however, the extrusion rates were reduced to 14/9/9 rpm to produce a thickness of 0.8890 mm (35 mils) and a weight of 1000 g/m^2. A thickness of 0.9144-0.9652 mm (36-38 mils) produced a weight of 1131 g/m^2. This produced a very good bond on the melting point bar and was also tried between two pieces of lining. Extrusion pressure on the PETG extruder was 11.6 Mpa (1678 psi), the Tone A was 3.4 Mpa (499 psi) and the Tone C was 2.2 Mpa (313 psi).

EXAMPLE 14

[0041] This example was prepared in accordance with Example 13, however, the extrusion rates were reduced to 12/8/8 rpm to produce sheets of 0,7620 (30 mils) thickness. The extruder pressure was 11.3 Mpa (1643 psi) for the PETG, and 3.3 Mpa (472 psi) and 1.9 Mpa (279 psi) for the A and C Tone extruders respectively. The melt temperature was set at 202.2°C (396°F). The roll speed remained at 7.5 fpm. The die gap was set at 0,7620 mm (30 mils). This produced sheets with a thickness of 0,8128 mm (32 mils) and a weight of 964 g/m^2. Sheets were also produced with a thickness of 0,6350-0,7112 (25-28 mils) and a weight of 762 g/m^2.

EXAMPLE 15

[0042] This example was prepared in accordance with Example 14, however, the extrusion rates were reduced to 10/7/7 rpm to obtain a sheet with a thickness of 0,5842-06350 mm (23-25 mils). This produced very good bonds when tested on the melting point bar. The extrusion pressure for the PETG extruder was 9.1 Mpa (1314 psi) and the Tone A and Tone C extruders were at 3 Mpa (432 psi) and at 1.7 Mpa (243 psi) respectively. The melt temperature was set 202.2 °C (396°F) and the roll speed remained at 7.5 fpm.

EXAMPLE 16

[0043] This example was prepared in accordance with Example 15, however, the extrusion rates were reduced to 8/6/6 rpm to obtain sheets with a 0,5080 mm (20 mils) thickness. Also, the extrusion rates were set at 9/6/6 rpm to obtain sheets with a thickness of around 0.4318-0.5080 mm (17-20 mils), this produced very good bonds when tested on the melting point bar. At a thickness of 0,4064-0.5388 mm (16-22 mils) sheets were produced with a weight of 508 g/m^2. Table III and IV below shows the dome test results for Example 11-16 above.

Table III Dome Test Results for a Examples 11-16

Material PETG/Tone	90/10	90/10	90/10	90/10	90/10
Thickness (mils)	32	40	17	41-42	49-50
Thickness (mm)	0.81	1.01	0.43	1.04-1.07	1.24-1.27
Weight (kg/m^2)	964	1273	523	1297	1592
1st Collapse (kg)	10.1	20.4	3.2	20.0	43.1
10th Collapse (kg)	10.0	16.2	2.3	16.3	25.8
% Resiliency	99	79	72	82	60
Mold Time	7	7	6	6	9

Table IV Dome Test Results for a Examples 11-16

Material PETG/Tone	90/10	90/10	90/10	90/10	90/10
Thickness (mils)	34-37	46-50	47-51	36-38	36-39
Thickness (mm)	0.86-0.94	1.17-1.27	1.19-1.29	0.91-0.96	0.91-0.99
Weight (kg/m^2)	1089	1561	1541	1152	1164
1st Collapse (kg)	12.0	31.6	35.5	16.1	17.0
10th Collapse (kg)	11.6	24.2	25.6	15.1	15.1
% Resiliency	997	77	72	94	89
Mold Time	7	7	9	7	7

EXAMPLE 17

[0044] This example was prepared in accordance with Example 16. The extruders remained at 9/7/7 rpm, but the die temperature was raised to 232.2°C (450°F) and the PETG extruder temperature profile was set at 162.8°C, 218.3°C, 232.2°C, 232.2°C and 232.2°C (325°F, 425°F, 450°F, 450°F and 450°F). The extrusion pressure was 9.6 Mpa (1394 psi) for the PETG extruder and 3 Mpa (440 psi) and 1.7 Mpa (250 psi) for the Tone A and Tone C extruders respectively. The Tone extruders remained at the prior temperature profiles. This reduced the die lines from the Tone. Also, this did not result in the Tone mixing into the PETG. Additionally, this yielded a good viscosity for the Tone, there was no roll sticking and the material had good bonding characteristics.

EXAMPLE 18

[0045] This example was prepared in accordance with Example 17, however at higher temperatures the edges of the sheet from the PETG got very runny and the extrusion rates were set to 14/9/9 rpm to obtain 0.8890 mm (35-mil) sheets. This produced no die score lines.

EXAMPLE 19

[0046] This example was prepared in accordance with Example 18, however polyethylene terephthalate (PET) (pre-dried) was used in place of PETG. The temperature profile on the extruder (which had previously been used for the PETG) was increased to 162.8°C, 218.3°C, 232.2°C, 232.2°C and 232.2°C (325°F, 425°F, 450°F, 450°F and 450°F) and the die temperature was set at 232.2°C (450°F). The extruders were set at 14/9/9 rpms. The temperature profile for the Tone extruders was set at 79.4°C, 176.7°C and 176.7°C (175°F, 350°F and 350°F) and the temperature for the melt pipe was set at 204.4°C (400°F). This produced sheets with thicknesses of 0.4064-0.5080 mm (16-20 mils) and 0.5588-0.6350 mm (22-25 mils). This produced nonuniform coating and no die score lines from the Tone.

EXAMPLE 20

[0047] This example was prepared in accordance with Example 19, however the PET extruder temperature was increased to 260°C (500°F) and the die temperature was increased to 260°C (500°F). The extrusion rate was set at 24/12/12 rpms, the extrusion pressures of the PET was 1.3 Mpa (193 psi), and 4 Mpa (591 psi) and 2.4 Mpa (354 psi) for the Tone A and Tone C extruders respectively. The melt temperature was set at 148.9°C (300°F). The flow was not good, but there were no score lines in the Tone coating.

EXAMPLE 21

[0048] This example was prepared in accordance with Example 20, however the temperature was increased to 287.8°C (550°F) for the die and for the co-extrusion block. The PET extruder temperature profile was set at 232.2°C, 260°C, 260°C, 260°C and 260°C (450°F, 500°F, 500°F, 500°F and 500°F). The PET melt pipe temperature was set at 287.8°C (550°F). The temperature profile for the Tone extruders were set at 79.4°C, 176.7°C and 176.7°C (175°F, 350°F and 350°F), and the pipe temperature was set at 148.9°C (300°F). The extruders were set at 14/9/9 rpms. The Tone exiting the lip was somewhere between 148.9°C and 287.8°C (300°F and 550°F) and showed no score die lines.

EXAMPLE 22

[0049] This example was prepared in accordance with Example 21, however the extruders flow rate was increased to 24/15/15 rpms resulting in 43.65 kg (97#)/hr total output. This rate was then reduced to 24/12/12 rpms and the sheets were placed on casting rolls. The extruder pressure was 1 Mpa (144 psi) for the PET and 4 Mpa (596 psi) and 2.3 Mpa (340 psi) for the Tone A and Tone C extruders respectively. The roll speed remained at 7.5 fpm. This resulted in a good surface look and very good Tone coating with very good bonding. The gauge was around 0.7366/0.7874 mm (29/31 mils) and 1000 g/m^2. The very high temperature did not hurt the flow of the Tone and eliminated the Tone die score lines. The sheet looked very good and resulted in a width of 27 cm (10 5/8 inches), where the Tone coated section was 23.19 cm (9 1/8 inches). Material with a thickness of 0.8890/0.9144 mm (35/36 mils) had a weight of around 1200 g/m^2. With the rolls temperature set at 12.8°C (55°F) there was no sticking. The coated sections were tough and flexible. The total output was around 50.4 kg (112 #/)hr with a Tone percent of around 20%. The Gauge was 0.8636-0.9144 mm (34-36 mils) and the weight was 1118 g/m^2. Table V below shows the dome test results for Example 22.

Table V Dome Test Results For a Sample Molded at 180°C for 2 minutes

PET/TONE	80/20
Thickness (mils)	33-34
Thickness (mm)	0.84-0.86
Weight (kg/m^2)	1081
1st Collapse (kg)	13.1
10th Collapse (kg)	12.9
% Resiliency	98

EXAMPLE 23

[0050] An ABA structure was made with Eastman GP001 polyester with a softening point of 74°C (165°F) and EMAC® 2260 ethylene methyl acrylate polymer. The adhesive two outer layers were the EMAC and the core was the GP001. A three-extruder coextrusion block system was used. The GP001 was extruded through a 5.08 cm (2 inch) Davis Standard extruder at 221.1°C (430°F) and the EMAC® through two 3.17 cm (1¼ inch) Davis Standard extruders at 232.2°C (450°F). The die temperature was 215.6°C (420°F) and a 55.88 cm (22-inch) die was used. The GP001 was predried before extrusion. The extrudate was cast onto a three roll casting system with the extrudate going onto the middle roll. Adjusting the die and the middle extruder's speed formed various sheet thicknesses. Sheets were produced that were 0.5080, 0.6350, 0.7366, 0.8890, 1.1430 and 1.2700 mm (20, 25, 29, 35, 45 and 50 mils) thick. The table below lists the dome test results on the sheets produced. The total of the A layers represented 18% of the total thickness of the finished sheet. The Dome test results of 5 molded at 95°C for 8 minutes in accordance with Example 23 are shown in Table VI below. The dome test results of 1 sample molded at 100°C for seven minutes in accordance with Example 23 is shown in Table VII below.

Table VI Dome Test Results for a Sample Molded at 95°C for 8 Minutes

Sample	**A**	**B**	**C**	**D**	**E**
Thickness (mm)	0.4826	0.6096-0.6350	0.6858-0.7366	1.1176-1.2192	1.2192-1.2700
(Thickness (mils)	19	24-25	27-29	44-48	48-50)
Weight (kg/m^2)	587	761	874	1436	1529
1st Collapse (kg)	2.2	4.4	6.7	30.0	37.3
10th Collapse (kg)	2.1	4.1	6.4	21.0	21.8
% Resiliency	95	93	96	70	58

Table VII Dome Test Results For a Sample Molded at 100°C for 7 minutes

Sample	35
Thickness (mm)	0.8890-0.9652
(Thickness (mils)	35-38)
Weight (kg/m^2)	1140
1st Collapse (kg)	15.1
10th Collapse (kg)	14.3
% Resiliency	95

EXAMPLE 24

[0051] This example was prepared in accordance with Example 23, except that the ABA structure used as the "A" layers a blend of 55% Tone and 45% GP001. The dome test data is recorded in Table VIII below. All samples displayed good adhesive properties.

Table VIII Dome Test Results For Samples Molded at 100°C for 7 Minutes

Sample	**A**	**B**	**C**
Thickness (mils)	25-26	34-36	45-47
Thickness (mm)	0.63-0.66	0.86-0.91	1.14-1.19
Weight (kg/m^2)	820	1116	1427
1st Collapse (kg)	8.9	18	34
10th Collapse (kg)	8.4	15.8	23.6

(continued)

Sample	A	B	C
% Resiliency	94	88	69

EXAMPLE 25

[0052] This example uses the same conditions and equipment as in Example 23, but the "A" layers are a blend of 55% Tone and 45% EMAC 2260. The dome data is shown in Table IX below. All samples showed good adhesive properties.

Table IX Dome Test Results For Samples Molded at 100°C for 7 Minutes

Sample	D	E	F
Thickness (mils)	45-47	35-36	25-26
Thickness (mm)	1.14-1.19	0.89-0.91	0.63-0.66
Weight (kg/m^2)	1399	1108	770
1st Collapse (kg)	27.3	14.2	5.1
10th Collapse (kg)	20.2	12.6	6.1
% Resiliency	74	89	119

Claims

1. A sheet stiffener material for use in footwear comprising one step extrusion-combined low melting point plastic adhesive resin and stiffening plastic resin, wherein said sheet stiffener material is stiff, resilient, has adhesive properties wherein it has an adhesive layer on two sides of the stiffening plastic resin without the low melting point resin being fully dissolved in the stiffening plastic resin, **characterized in that** the stiffening resin comprises a polyethylene terephthalate glycol copolyester and the lower melting point adhesive resin comprise a polycaprolactone resin.

2. A stiffener material according to claim 1, where the lower melting point adhesive resin is a polycaprolactone resin and the stiffening resin is a polyethylene terephthalate glycol copolyester.

3. A stiffener material according to claim 2, wherein the ratio of polyethylene terraphthalate glycol copolyester/polycaprolactone is from about 70/30 to about 95/5.

4. A process for preparing a stiffener material for use in footwear in accordance with one of claims 1 to 3, comprising combining a low melting point plastic adhesive resin and a stiffening plastic resin in a single step to produce a stiffening material, wherein said stiffening material is stiff, resilient and has adhesive properties, and wherein said low melting point plastic adhesive and said stiffening plastic resin are coextruded to form a sheet of stiffening material with a plastic resin core, wherein said core further comprises an exterior layer of a low melting point plastic adhesive resin.

5. The process according to claim 4, wherein the materials are coexruded through either a coextrusion block or a manifold sheeting die.

Patentansprüche

1. Bahnversteifungsmaterial zur Verwendung in Schuhen; umfassend in einem Schritt extrusionsverbundenes Kunststoffhaftmittelharz mit niedrigem Schmelzpunkt und Versteifungskunststoffharz, wobei das Bahnversteifungsmaterial steif und federnd ist und Haftmitteleigenschaften aufweist, wobei es eine Haftmittelschicht auf zwei Seiten des Versteifungskunststoffharzes aufweist, wobei das Harz mit niedrigem Schmelzpunkt nicht vollständig in dem Versteifungskunststoffharz gelöst ist, **dadurch gekennzeichnet, dass** das Versteifungsharz einen Polyethylenereph-

thalatglykolcopolyester umfasst und das Haftmittelharz mit niedrigerem Schmelzpunkt ein Polycaprolactonharz umfasst.

2. Versteifungsmaterial nach Anspruch 1, wobei das Haftmittelharz mit niedrigerem Schmelzpunkt ein Polycaprolactonharz ist und das Versteifungsharz ein Polyethylenterephthalatglykolcopolyester ist.

3. Versteifungsmaterial nach Anspruch 2, wobei das Verhältnis von Polyethylenterephthalatglykolcopolyester/Polycaprolacton von etwa 70/30 bis etwa 95/5 beträgt.

4. Verfahren zur Herstellung eines Versteifungsmaterials zur Verwendung in Schuhen gemäß einem der Ansprüche 1 bis 3, umfassend das Verbinden eines Kunststoffhaftmittelharzes mit niedrigem Schmelzpunkt und eines Versteifungskunststoffharzes in einem einzelnen Schritt zur Herstellung eines Versteifungsmaterials, wobei das Versteifungsmaterial steif und federnd ist und Haftmitteleigenschaften aufweist, und wobei das Kunststoffhaftmittel mit niedrigem Schmelzpunkt und das Versteifungskunststoffharz coextrudiert werden, um eine Bahn von Versteifungsmaterial mit einem Kunststoffharzkern zu bilden, wobei der Kern weiter eine Außenschicht eines Kunststoffhaftmittelharzes mit niedrigem Schmelzpunkt umfasst.

5. Verfahren nach Anspruch 4, wobei die Materialien durch entweder einen Coextrusionsblock oder eine Manifoldbahndüse coextrudiert werden.

Revendications

1. Un élément de renforcement en forme de feuille à utiliser dans des chaussures comprenant une résine adhésive plastique à bas point de fusion et une résine plastique de renforcement combinées par extrusion en une étape, dans lequel ledit élément de renforcement en forme de feuille est rigide, résilient, possède des propriétés adhésives, dans lequel il a une couche adhésive sur deux côtés de la résine plastique de renforcement sans que la résine à bas point de fusion soit entièrement dissoute dans la résine plastique de renforcement, **caractérisé en ce que** la résine de renforcement comprend un copolyester glycol de polyéthylène téréphtalate et la résine adhésive à plus bas point de fusion comprend une résine de polycaprolactone.

2. Un élément de renforcement selon la revendication 1, où la résine adhésive à plus bas point de fusion est une résine de polycaprolactone et la résine de renforcement est un copolyester de polyéthylène téréphtalate glycol.

3. Un élément de renforcement selon la revendication 2, dans lequel le rapport copolyester de polyéthylène téréphtalate glycol /polycaprolactone est d'environ 70/30 à environ 95/5.

4. Un procédé pour préparer un élément de renforcement à utiliser dans des chaussures conformément à l'une des revendications de 1 à 3, comprenant la combinaison d'une résine adhésive plastique à bas point de fusion et une résine plastique de renforcement en une seule étape pour produire un élément de renforcement, dans lequel ledit élément de renforcement est rigide, résilient et a des propriétés adhésives, et dans lequel ledit adhésif plastique à bas point de fusion et ladite résine plastique de renforcement sont coextrudés pour former une feuille d'un élément de renforcement avec une âme en résine plastique, dans lequel ladite âme comprend par ailleurs une couche extérieure d'une résine adhésive plastique à bas point de fusion.

5. Le procédé selon la revendication 4, dans lequel les éléments sont coextrudés au moyen soit d'un bloc de coextrusion soit d'une matrice de feuille.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 3523103 A **[0002]**
- US 3590411 A **[0002]**
- US 3647616 A **[0002]**
- US 3891785 A **[0002]**
- US 3973285 A **[0002]**
- US 4814037 A **[0002]**
- US 6391380 B **[0002]**
- US 6475619 B **[0002]**
- WO 03066329 A1 **[0003]**
- WO 0172162 A1 **[0003]**
- GB 2291880 A **[0003]**
- WO 0030485 A **[0003]**
- FR 2623980 **[0003]**
- US 5532066 A **[0003]**
- EP 0364301 A **[0003]**