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10,357,909
July 23, 2019

Thermoset in-mold finishing film

Abstract

This invention relates to the manufacturing of durable thermoset in-mold finishing films (TIMFFs) combining in-mold decorating and in-mold durable exterior grade coating capabilities, to molded articles having TIMFFs adhering to their surfaces and both showing a decoration and providing protection, and to thermosetting resin formulations used in the manufacturing of TIMFFs. In some embodiments, the thermoset is prepared via polyurethane chemistry; the manufacturing process comprises reaction injection molding (RIM) with a specially designed mold; and articles having TIMFFs adhering to their surfaces include graphic panels for durable signage, structural graphics, molded flooring, prefabricated housing, aerospace structures and body panels, automotive structures and body panels, and marine structures and body panels. In addition to RIM, the TIMFF technology is also compatible with other processes, such as injection molding, compression molding, resin transfer molding, spin casting, rotational molding, thermoforming, roll lamination, use of a platen/laminate press, and blow molding.

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Parent Case Text

The present application claims priority benefit from U.S. Provisional Patent Application No. 62/005,103, filed May 30, 2014, the entire subject matter of which is hereby incorporated herein by reference in its entirety.

1. A method for manufacturing an in-mold decorated and in-mold coated thermoset article, said method comprising: (A) placing, on casting paper or texture plate, a durable coating film that is a third B-stage polyurethane resin, said third B-stage polyurethane resin optionally containing an additive, a finish, or a combination or mixture thereof, selected to enhance the durability of the coated surface of the finished article by improving its scratch resistance, wherein the casting paper or texture plate are located in a mold; (B) applying a printable film comprising a reactive and printable resin to the durable coating film, thereby to form the printable film, where (i) said reactive and printable resin is a first B-stage polyurethane resin and a second B-stage polyurethane resin; (C) optionally printing an image, pattern, text, indicia, or combination thereof onto said printable resin; (D) filling the mold with an article resin, the article resin is a fourth B-stage polyurethane resin; and (E) performing a curing reaction to thereby form an integrally bonded molded article.
2. The method of claim 1, wherein the step of performing a curing reaction comprises a step of performing a curing reaction under a first curing reaction condition to create a partially crosslinked state.
3. The method of claim 2, where the step of performing a curing reaction further comprises a step of performing a second curing reaction under a second curing reaction condition to create a fully crosslinked state of the unsupported laminate film and the article resin.
4. The method of claim 1, where placing of the durable coating film on casting paper or texture plate is performed by using a method selected from the group consisting of solvent mixing and casting, or extrusion mixing and casting, or a combination thereof.
5. The method of claim 1, where the first B-stage polyurethane resin is clear or contains an additive that makes it white and opaque; said additive is selected from the group consisting of cellulosic additives, talc, ultra-white alumina trihydrate, white glass powder, titanium white, and combinations or mixtures thereof.
6. The method of claim 1, where said printing on said first B-stage polyurethane resin is performed by using a technique selected from the group consisting of digital printing, flatbed printing, UV printing, gravure printing, screen printing, offset printing, offset lithography, inkjet printing, engraving, reprography, thermographic printing, flexography, and combinations or sequences thereof.
7. The method of claim 1, where said optional additive that enhances the scratch resistance of said durable coating film is aluminum oxide.
8. The method of claim 1, where the first B-stage polyurethane resin, the second B-stage polyurethane resin, the third B-stage polyurethane resin and the forth B-stage polyurethane resin may comprise an optional additional ingredient chosen from the group consisting of reinforcing agents, impact modifiers, antistatic agents, fire retardants, antioxidants, UV stabilizers, photoinitiators, thermal initiators, catalysts, inhibitors, buffers, dispersants, surfactants, stabilizers, compatibilizers, rheology modifiers, defoamers, drying agents, blowing agents, mold release agents, or any combination or mixture thereof.

9. The method of claim 1, where said molding process is selected from the group consisting of reaction injection molding, injection molding, compression molding, resin transfer molding, spin casting, rotational

11. The method of claim 1, wherein the first B-stage polyurethane resin, the third B-stage polyurethane resin and the fourth B-stage polyurethane resin are each semi-cured.

U.S. Patent Application No. 2010167045 discloses a reactive mixture for coating moldings via RIM, comprising at least 40% by weight of (meth)acrylates having at least two double bonds, the reactive mixture comprising at least one photoinitiator and at least one thermal initiator. It also describes a coated molding comprising a molding which is obtainable by injection molding processes and comprises at least one polymer selected from the group consisting of poly(methyl methacrylate), polymethylmethacrylimide, styrene-acrylonitrile copolymer, styrene-maleic acid copolymer and poly(methyl methacrylate) copolymers, and a coating which is obtainable by polymerization of (meth)acrylates having at least two double bonds, the coating having an adhesive strength rating of not more than 1 according to the cross-hatch test and a decrease in gloss at 20.degree. C. after a scratch resistance test according to ASTM D1044 (12/05) (applied weight

C. Decorating Compositions and Processes

U.S. Pat. No. 6,652,983 discloses a method for thermoplastic IMD whereby a decorating sheet is set in an injection mold and, after clamping the mold, molten molding resin is injected into the mold and allowed to cool and solidify. A portion of the in-mold decorating sheet becomes integrally bonded to a surface of the molding resin so that a decorated molded resin product is obtained. The decorative sheet has strong adhesion to the surface of the molded resin product over the area where they are integrally bonded, while being sufficiently brittle to enable the easy trimming of any unnecessary portion (any portion which had not become integrally bonded to the surface of the molding resin) from the surface of the molded resin product.

U.S. Pat. No. 8,968,618 discloses a method of making a molded article having a curved surface, such as plates or serving trays, and the resulting molded articles. The in-mold label is a laminated film that includes a backing layer, a printed surface incorporating one or more designs thereon, a protective film layer, and one or more notches each having adjacent edges separated by a gap of predetermined distance and configured to intersect to ensure conformance of the in-mold label to the angled or curved peripheral portion of the article.

U.S. Patent Application No. 20070184148 exemplifies patents disclosing novel mold constructions to improve the efficiency of thermoplastic IMD processes and to thus achieve lower manufacturing costs and shorter delivery periods. By contrast, mold construction does not appear to have received much attention for thermoset IMD processes.

U.S. Patent Application No. 20080152855 discloses a composition suitable for the formation of a release layer between the durable layer and the carrier layer in an IMD or thermal transfer printing process, and a process for the formation of a release layer comprising dispersing or dissolving the release layer composition in a solvent followed by curing this composition.

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apparatus which prevents the use of a pattern having a defect so as to improve the yield of a decorative molding process. This process involves the use of inspection equipment containing a sensor that measures the transmission and reflection of light and thus identifies defects in the transfer layer optically. It then marks the defective portions of the transfer sheet. The use of defective portions of the transfer sheet during simultaneous molding/decoration can thus be avoided by skipping these portions containing defective patterns.

U.S. Patent Application No. 2010196651 discloses an object having a functional element embedded in its top surface and processes for its manufacturing. The object is in general formed by molding, stamping, lamination or a combination thereof. The functional element includes any electrical or mechanical elements that are capable of performing a function.

U.S. Patent Application No. 2010291329 discloses an in-mold label comprising a polymeric or cellulosic carrier base film (1) having a first decorative surface (1a) and a second, backing surface (1b), said label comprising a pattern (3) printed on said first decorative surface (1a) thereof, said printed first surface (1a) being laminated with a transparent protective top film (2), affixed thereto by means of an adhesive (4), the printed pattern (3) being visible through said transparent protective top film (2). It also discloses a method for manufacturing such a label and a method for incorporating it onto the surface of a polymeric article.

World Patent Application No. WO2012065966 discloses a process for overlaying a base substance with a multilayer decorative film in a thermoforming process, preferably in a vacuum forming process, wherein the process comprises the steps of (i) providing a multilayer decorative film comprising a hard coat layer (A), an adhesive layer (D), a base film layer (B) and optionally a design layer (C) between these layers (A) and (D), wherein the adhesive layer (D) comprises at least one latent reactive adhesive, (ii) applying the adhesive layer (D) of the decorative film to the surface of a base substance, and (iii) overlaying the base substance with the decorative film by heating at 70.degree. C. or more. The resulting multilayer decorative films are claimed to have a degree of elongation of 10 to 1000% (preferably 50 to 1000%), a tensile strength of 50 to 1000 kg/cm.sup.2, a processing temperature of 70 to 220.degree. C. (preferably 70 to 200.degree. C.), adhesiveness of 50 N/25 mm or more, and durability of 1 week or more at 80.degree. C. and 98% relative humidity.

Chinese Patent No. CN102673293 discloses thermal transfer IMD and a preparation method thereof that enable the high-resolution (600 dots per inch) printing of a PET film sheet, with the possibility of printing continuous patterns and gradient patterns, and color printing with high transparency and high transmittance on the PET back surface. Color saturation is high. The adhesion of a graphic ink layer and a PET film is strong. The decoration can survive high temperatures, can extend while the PET film is extended in a 3D thermal forming process, and has high extension. The extended surface is completed; the ink layer cannot be broken and has no wrinkles. The method not only can realize large-scale continuous production, but it can also overcome the shortcoming that hot-melt resin of the ink coating layer cannot survive high temperatures during the molding process. Products obtained by using the method cannot flush ink and glue and have complete patterns. These patterns manifest high gloss, anti-friction, anti-scratch, and weather resistance, so that they are durable. For example, biaxially oriented PET (BOPET) film was used as the carrier film, an adhesive was formulated, inks of various colors were used to create a pattern, and thermal transfer and injection molding were performed to transfer the pattern onto a PET substrate and to thus obtain a high-resolution printed PET film.

Chinese Patent No. CN102744939 discloses a thermoset IMD film and a preparation method thereof. The IMD film comprises a PET base film whose upper surface is provided with a scratch-resistant thermoset coating layer. An ink adhesion layer is provided on the lower surface of the PET base film. Adhesion of the ink layer on the film layer is provided. The preparation method comprises the steps of performing corona treatment on the PET base film; coating the PET base film; drying the coated PET base film; thermally curing the dried coated PET base film; coating the ink adhesion layer on the back of the cured dried coated PET base film; curing the PET film of which the back is coated with the ink adhesion layer; and rolling and cutting the film. The coating is strengthened by raising the temperature gradually to complete its crosslinking. The resulting thermoset IMD film has high transmittance, flexibility, and adhesion.

World Patent Application No. WO2014025005 discloses a multilayer film which has excellent surface hardness, excellent transparency, small thermal shrinkage, and high brittleness; and which (because it is

U.S. Patent Application No. 2012315447 discloses a label for in-mold molding, which comprises a laminate film comprising a substrate layer (A) and a heat-sealable resin layer (B), wherein the substrate layer (A) comprises a thermoplastic resin in an amount of from 40 to 90% by weight and at least one of an inorganic fine powder and an organic filler in an amount of from 10 to 60% by weight, and the heat-sealable resin layer (B) comprises a thermoplastic resin in an amount of from 50 to 100% by weight.

D. Limitations of Existing IMC and IMD Technologies Using RIM

(1) A method of decorating with printed images does not currently exist for the RIM process, and, in fact, for any other reactive molding process either. Since IMD is performed by using thermoplastic resins that are transferred to the molded article, this is not a viable method for RIM which uses reactive precursors that cure via exothermic reactions into thermoset resins. IMD for RIM is currently more of an in-mold painting system as it is limited to two-part polyurethane paint that covers over the entire article.

(3) The white layer presents another potential issue. The resin color of a molded article affects the color of the ink layer. In general, the decoration will be more visible and vibrant if the resin color is lighter. For thermoplastic IMD, white can be printed under the other colors as the ink formulation allows the image to be transferred or bonded to the molded article. The exothermic reaction occurring during the RIM process will not allow a printed image or white layer as only a two-part gel coat which is not compatible with any printable system can be used with existing thermoset IMC and IMD technologies using RIM.

(5) While much work has been done to design optimum molds for thermoplastic IMC and IMD, little work has been done to design optimum molds for thermoset IMC and IMD via RIM.

It can be seen from the discussion above that a new combined IMC and IMD technology which alleviates some of these limitations of current thermoset IMC and IMD technologies that use RIM would be a significant development with many potential applications.

SUMMARY OF THE INVENTION

In one aspect, the invention comprises a method for manufacturing an in-mold decorated and in-mold coated thermoset article, said method comprising: (A) placing, on a first carrier film, a printable film comprising a reactive resin and a printable resin, where (i) said reactive resin is a first B-stage resin (binder) and (ii) said printable resin is a second B-stage resin which either is clear or contains an additive that makes it white and opaque; (B) printing an image, pattern, text, indicia, or combination thereof onto said printable resin; (C) placing, on a second carrier film, a durable coating film that is a third B-stage resin, said resin optionally

In another aspect, the invention comprises a method for manufacturing an in-mold decorated and in-mold coated thermoset article, said method comprising: (A) placing, on a first carrier film, a printable film comprising a reactive resin and a printable resin, where (i) said reactive resin is a first B-stage resin (binder) and (ii) said printable resin is a second B-stage resin which either is clear or contains an additive that makes it white and opaque; (B) printing an image, pattern, text, indicia, or combination thereof onto said printable resin; (C) placing, on a second carrier film, a durable coating film that is a third B-stage resin, said resin optionally containing an additive, a finish, or a combination or mixture thereof, selected to enhance the durability of the coated surface of the finished article by improving its scratch resistance; and (D) combining said printable film on the first carrier film and said durable coating film on the second carrier film into a multilayer laminate film on a roll laminator to thereby form a laminate film. In some implementations of this aspect of the invention, the method optionally further comprises the steps of (E) loading said laminate film into a device that assists in the removal of the first carrier film and the second carrier film to thereby form an unsupported laminate film and sets the unsupported laminate film into a mold; (F) filling the mold with an article resin; and (G) performing a curing reaction.

In yet another aspect, the invention comprises a method for manufacturing an in-mold decorated and in-mold coated thermoset article, said method comprising: (A) loading a laminate film into a device, said laminate film comprising a printable film on a first carrier film and a durable coating film on a second carrier film, wherein said device assists in the removal of the first carrier film and the second carrier film to thereby form an unsupported laminate film and sets the unsupported laminate film into a mold; (B) filling the mold with an article resin; (C) performing a curing reaction.

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In yet another aspect, the invention comprises an in-mold decorated and in-mold coated molded thermoset article, satisfying the limitations set forth for any of the aspects of the invention cited above, where said article is a solid thermoset elastomer, a rigid thermoset, or a structural foam.

In yet another aspect, the invention comprises an in-mold decorated and in-mold coated molded thermoset article comprising a single layer of resin selected from the group consisting of polyurethanes, polyureas, poly(urethane urea)s, and combinations or mixtures thereof, wherein the article has a three-dimensional shape with a design integral to the three-dimensional shape, and wherein the design is selected from the group consisting of texture, color, decoration or combination thereof. In some embodiments, the article is selected from the group consisting of graphic panel for durable signage and structural graphics, a molded flooring product, a prefabricated housing wall or roof component, or a structure or body panel in a transportation vehicle. The three-dimensional shape is non-planar in some embodiments and planar in some other embodiments. The design is clear in some embodiments and opaque in some other embodiments.

The accompanying drawings, which are included to provide further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

FIG. 2 is a schematic illustration of additional details of a non-limiting embodiment of the print (decoration) film component of a TIMFF.

FIG. 4 is a schematic illustration of the integrally bonded molded article and the TIMFF of FIG. 1 after the completion of the molding process.

FIGS. 6A-6C provide schematic illustrations of two non-limiting examples of the mold system of a RIM apparatus that may be used in the manufacturing process, FIG. 6A illustrates a Table top/clamp method, FIG. 6B illustrates an enlarged view of the Table top of FIG. 6A; and FIG. 6C illustrates a Platen-press method.

FIG. 8 provides a detailed closed-panel view of the mold in another embodiment of the invention.

FIGS. 9A and 9B are a schematic illustration of Stage 1 of the curing process according to an embodiment of

FIGS. 10A and 10B are a schematic illustration of Stage 2 of the curing process according to an embodiment of the invention in which curing occurs in two stages, wherein FIG. 10A illustrates the Table top/clamp method prior to Stage 2 of the curing process and FIG. 10B illustrates layer 205 during Stage 2 of the curing process.

FIG. 12 is a schematic illustration of the thermoset in-mold finishing film (TIMFF) and reaction injection molding (RIM) production flow according to another embodiment of the invention.

FIGS. 13A-13D compare some details of embodiments using direct extrusion to a texture plate and embodiments using a roller, wherein FIG. 13A illustrates a device for direct extrusion onto a texture plate, FIG. 13B illustrates a detailed view of extruder 405, FIG. 13C illustrates a roller device and FIG. 13D illustrates a detailed view of the extruder producing sheet 6.

FIGS. 14A-14C show the details of one possible equipment layout that may be used in manufacturing embodiments of the invention by the method described in Example 2, wherein FIG. 14A illustrates an extruder device coupled to a roller 406 and release liners 407 and 408, FIG. 14B illustrates a device for incorporation of a white print and release liner, and FIG. 14C illustrates a detailed view of the white print and release liner option.

FIGS. 15A-15D show the details of another possible equipment layout that may be used in manufacturing embodiments of the invention by the method described in Example 2, where FIG. 15A illustrates a screw extruder coupled to a TIMFF extrusion molding die 701, FIG. 15B illustrates a detailed view of the extrusion molding die 701, FIG. 15C illustrates a view of the extrusion molding die 701 with resin filing the mold and FIG. 15D illustrates a product following molding and projected from the extrusion molding die 701.

FIGS. 16A and 16B illustrate a completed in-mold coated and in-mold decorated article that may be manufactured by using the equipment layout shown in FIGS. 15A-15D, wherein FIG. 16A illustrates an in-mold coated and in-mold decorated article projected from the extrusion molding die 701 and FIG. 16B illustrates a completed in-mold coated and in-mold decorated article.

FIGS. 17A-17C show some of the details of yet another possible equipment layout that may be used in manufacturing embodiments of the invention by the method described in Example 2, where FIG. 17A illustrates an extruded coated resin on a flexible texture plate; FIG. 17B illustrates TIMFF and texture plate rolled into a mold and FIG. 17C illustrates TIMFF and texture plate in a tube/pipe mold.

FIGS. 18A-18C show further details of the manufacturing of embodiments of the invention according to the method illustrated in FIGS. 17A-17C as well as illustrating a completed in-mold coated and in-mold decorated article that may be manufactured by using this method where FIG. 18A illustrates a device for making a mold coated and in-mold decorated article with a dispenser system 808, a spin molding chamber 806 and a motor 807 to operate the spin molding chamber, FIG. 18B illustrates a demold graphic tube/pipe, and FIG. 18C illustrates a tube or pipe with TIMFF and decoration.

DETAILED DESCRIPTION OF THE INVENTION

While the invention is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and will be described in detail herein. It should be understood, however, that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims. To that extent, elements and limitations that are disclosed herein, for example, in the Abstract, Summary of the Invention, Detailed Description of the Invention, and Some Envisioned Applications of TIMFF sections, but not explicitly set forth in the claims, should not be incorporated into the claims, singly or collectively, by implication, inference or otherwise.

In some embodiments, the printable film and the durable coating film are prepared from thermosetting resin formulations belonging to the same polymer family. In some other embodiments, the printable film and the durable coating film are prepared from thermosetting resin formulations belonging to different polymer families. In implementations of the invention using printable film and durable coating film materials of different families, the different families must have compatible chemistries; in other words, the formulation ingredients for the selected families must be capable of curing together into an integral TIMFF manifesting adhesion between the printable film and the durable coating film.

In some embodiments, some or all of the ingredients of the article resin originate from biobased feedstocks and/or from recycled polymer wastes, providing a more environmentally friendly alternative to a resin derived entirely from fossil fuel based virgin feedstocks.

In some embodiments, the printable resin may be clear or contain an additive that makes it white and opaque. In such an embodiment, the additive may include cellulosic additives, talc [hydrated magnesium silicate, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$], titanium white (titanium dioxide, TiO_2), ultra-white alumina trihydrate, white glass powder, antimony white (Sb_2O_3), barium sulfate (BaSO_4), white lead [$(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$], zinc white (ZnO), zinc sulfide (ZnS), and/or lithopone (a mixture of BaSO_4 and ZnS). Titanium white is the most widely used white pigment since it has an extremely high efficiency so that it can provide a white color even when used in a very small amount while not containing heavy metal elements. Some cellulosic fillers, talc, ultra-white alumina trihydrate and white glass powder are advantageous as whitening additives because they are environmentally friendly. In many embodiments of the invention, cellulosic fillers, talc, ultra-white alumina trihydrate, white glass powder, titanium white, and combinations or mixtures thereof will hence be used to make the printable resin white.

In some embodiments, the carrier film may be a suitable liner material including kraft paper, casting paper, silicone-coated paper, poly(vinyl chloride) (PVC), polyethylene, polypropylene, polystyrene, polyacrylates, polymethacrylates, polycarbonates, polyesters [such as, but not limited to, poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), and poly(ethylene furanoate) (PEF)], cellulose acetate, cellulose acetate butyrate, ethyl cellulose, and cellophane are non-limiting examples of liner materials.

Various methods may be used for placing the resin of a printable film and/or the resin of a durable coating film on a carrier film and/or release liner. In one embodiment, non-solvent extrusion of the resin of a printable film and/or the resin of a durable coating film may be used to place such resins on a carrier film and/or release liner. In another embodiment, solvent extrusion of the resin of a printable film and/or the resin of a durable coating film may be used to place such resins on a carrier film and/or release liner. In another embodiment, solvent formulation spray of the resin of a printable film and/or the resin of a durable coating

It is important to emphasize, also, that while many implementations of the invention use a carrier film, the use of a carrier film and/or release liner is not a limiting aspect of the invention since many other implementations of the invention do not use a carrier film and/or release liner. For example, a carrier film can be used in some implementations utilizing processes such as roll lamination or molding.

B. Embodiments Using Reaction Injection Molding and Polyurethane Chemistry

As a non-limiting example of PU compositions, the reaction of a hydroxyl group with an isocyanate provides a urethane linkage while the reaction of an amine group with an isocyanate provides a urea linkage. It is well-known to workers in the field of polyurethane materials that polymers with any percentage of urea linkages ranging from 0% to 100% relative to the total amount of urethane and urea linkages can be synthesized via polyurethane chemistry by varying the relative amounts of reactants containing hydroxyl groups and amine groups used to react with an isocyanate. This flexibility of polyurethane chemistry is commonly used by workers in the field as a design variable to fine-tune the performance attributes of a polymer to meet the needs of a targeted application.

Non-limiting examples of reactive precursor mixture ingredients used in polyurethane chemistry include: (a) Polyols (such as the many commercially available polyether polyols, polyester polyols, and polycarbonate polyols; differing in their compositions, average molecular weights, and numbers of reactive functionalities); (b) chain extenders containing hydroxyl reactive groups (such as ethylene glycol, diethylene glycol, 1,3-propanediol, 1,4-butanediol, and 1,6-hexanediol); (c) a chain extender (diethyltoluenediamine) containing amine reactive groups; (d) crosslinkers (such as glycerol and pentaerythritol); (e) aromatic isocyanates [such as the difunctional methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) and the polymeric MDIs (PMDIs) of higher functionality]; and (f) aliphatic isocyanates [such as methylene dicyclohexyl diisocyanate (H.sub.12MDI) which is the product of the hydrogenation of the phenyl rings of MDI, isophorone diisocyanate, and 1,6-hexamethylene diisocyanate].

Many major producers of aliphatic isocyanates are European companies, such as those that are members of the European Aliphatic Isocyanates Producers Association (as of the date of this disclosure, BASF, Bayer MaterialScience, Evonik Industries, and Vencorex France), whose product lines are good starting points in searching for aliphatic isocyanates for use in TIMFF film formulations. It can be seen from the website of this organization that, as of the date of this disclosure, the following were among the major product families offered by these companies: (a) monomeric diisocyanates (with the most readily available products being HDI, IPDI, and HMDI), (b) polyisocyanates (with the most readily available products being HDI trimer, HDI biuret, HDI uretdione, and IPDI trimer), and (c) blocked polyisocyanates (with HDI trimer or IPDI trimer blocked by 2-butanone oxime as representative products). Without limiting the generality of the invention, one way of obtaining B-stage PU film formulations where curing to different levels in different stages happens thermally and the final cured films have the desired mechanical properties is to use an optimized mixture of unblocked and blocked aliphatic isocyanates.

Polyurethane prepregs developed by Evonik and using aliphatic isocyanates (described in an article titled "Polyurethane Prepregs--A New Concept for CFRP Processing") may provide another formulation option in developing B-stage PU film formulations for the manufacture of embodiments of the invention.

Specific non-limiting examples of polyol and isocyanate product grades as well as other formulation ingredients used in the experimental work performed up to the date of this disclosure will be listed in the EXAMPLES section to facilitate the teaching of the invention.

In one embodiment, FIG. 1 is a schematic illustration of the sequence in which the components of a non-limiting example of a two-part TIMFF along with an article resin (which may, optionally, contain reinforcements) would be located inside the mold of a RIM apparatus. The following notation is used: 1: PU-type article resin which would be in contact with the top mold surface, 2: clear or white reactive (B-stage) PU resin that accelerates and/or assists the bonding of the TIMFF to the article resin as well as providing a surface to be printed upon, 3: optional corona and/or other surface treatment for component 2 to enhance its printability, 4: digital print or gravure UV ink or treated print layer (the decoration) placed on the surface of the print base layer 2 or on the optionally treated surface 3 of the print base layer, and 5: reactive (B-stage) PU resin that accelerates and/or assists in the bonding of the decorated print layer to the durable coating film 6 (such as an automotive-grade PU or PU/acrylate hybrid or fluoropolymer hardcoat layer) which would be

FIG. 2 is a schematic illustration of additional details of a non-limiting embodiment of the print (decoration) film component of a TIMFF. The following notation is used: 2: clear or white reactive (B-stage) PU resin that accelerates and/or assists the bonding of the TIMFF to the article resin as well as providing a surface to be printed upon, 3: optional corona and/or other surface treatment for component 2 to enhance its printability, 4: digital print or gravure UV ink or treated print layer (the decoration) placed on the surface of the print base layer 2 or on the optionally treated surface 3 of the print base layer, and 301: poly(ethylene terephthalate (PET) release liner that serves as the carrier film for both a reactive bonding resin layer and a reactive printable resin layer.

In FIGS. 1 and 2, a reactive PU bonding resin is a B-stage binder that begins crosslinking as it reacts to the exothermic reaction of the mold resin as it is injected into the mold. PU is a non-limiting example of a family of resins, suitable for use as binder resins, where the processing behavior as well as the end use performance characteristics can be varied over broad ranges by modifying the reactive precursor mixture used in polyurethane chemistry to meet different application requirements.

FIG. 3 is a schematic illustration of additional details of a non-limiting embodiment of the durable coating film component of a TIMFF. The following notation is used: 302: PET release liner that serves as the carrier film for the coating film, 5: B-stage reactive PU bonding resin layer formulated to impregnate the printable resin during lamination and to crosslink with it during molding, and 6: a PU or PU/acrylate hybrid or fluoropolymer hardcoat layer optionally containing additives and/or finishes selected to further enhance the durability of the coated surface. As a non-limiting example, the additive aluminum oxide can be used to provide an extremely durable finish to laminate floor panels by enhancing the scratch resistance of the coated surface.

FIG. 4 is a schematic illustration of the integrally bonded molded article and the TIMFF of FIG. 1 after the completion of the molding process. Here, 1A and 3A represent the top and bottom halves of the open mold respectively. Note that, in this particular non-limiting example, the bottom half of the mold has a curved shape which has been imparted to the molded article. The molded article and the TIMFF are integrally bonded to each other at the interface 2A.

FIG. 5 is a schematic illustration of a non-limiting example of the mix and dispenser system of a RIM apparatus that may be used in the manufacturing process. The following notation is used: 101: isocyanate feed tank, 102: isocyanate heat exchanger, 103: polyol heat exchanger, 104: nucleator, 105: stir motor, 106: polyol feed tank, 107: polyol metering piston and recirculation pump, 108: polyol supply line, 109: filler mix module, 110: recirculation mix head, 111: isocyanate supply line, 112: isocyanate metering piston and recirculation pump, 113: isocyanate return line, and 114: polyol return line.

FIGS. 6A-6C provide schematic illustrations of two non-limiting examples of the mold system of a RIM apparatus that may be used in the manufacturing process. (a) Table top/clamp method. (b) Platen-press method. The following notation is used: 201: top mold, 202: spacer (or gap) ring, 203: TIMFF film, 204: registration system (may optionally be a texture plate in some non-limiting embodiments), 205: bottom mold, 206: mold heater, 207: mold open/close actuator, and 511: frame of platen press in the example of the platen-press method. In both examples, the mold system combines three features. Firstly, the height of the top mold surface is adjustable to enable the fabrication of molded articles of different thicknesses. Secondly, the entire mold can optionally be tilted to some angle (such as, but not limited to, a tilt of 20.degree. C.) to facilitate the filling of the mold with resin. Thirdly, variable finish textures and designs appropriate for the article that is being manufactured can be placed on the platen face of the bottom surface of the mold and thus imprinted on the exposed surface of the in-mold decorated and in-mold coated molded article.

FIGS. 7A-7F provide more detailed open (a) and closed (b) views of the mold in FIG. 6. The following additional notation is used: 202-1: open area of spacer (or gap) ring, where the mold resin and reinforcements are injected, with the depth of the ring determining the thickness of the panel; 204-1: pin register hole; 205-1: and pin that registers into hole 204-1.

In some other embodiments of the invention, the curing that occurs during the RIM process can be summarized in terms of two stages (Stage 1 and Stage 2). In such embodiments, a first curing reaction condition prevails during Stage 1 and creates a partially crosslinked state, and then a second curing reaction condition prevails during Stage 2 to create a fully crosslinked state of the unsupported laminate film and the article resin. It should be remembered, in this context, that a B-stage resin is already partially cured; in other words, it is partially crosslinked relative to the starting formulation ingredients. Hence the curing that occurs during Stage 1 to create a partially crosslinked state refers to the further advancement of the extent of crosslinking starting from a state of the film where it is already partially crosslinked, to move further towards the fully cured state, which, however, is not reached until the end of Stage 2.

In such an embodiment, Stage 2 cure begins, approximately in the middle of the Stage 1 cure, when the bottom mold heater turns on and starts the Stage 2 cure. Optionally the pressure may be increased during the Stage 2 cure. Curing continues until the resins in the molded article and in the TIMFF have all cured completely. After the completion of the Stage 2 cure, the mold cools and then opens for article removal. The reaction injection molded article is now complete, with an ultra-durable IMD. This understanding of the Stage 2 cure is further illustrated schematically in FIGS. 10A-10B. Most of the notation has been introduced in FIGS. 1 and 6A-6C. The following additional elaborations are useful in understanding this drawing: 1: PU-type article resin which would be in contact with the top mold surface, 5: reactive (B-stage) PU resin that accelerates and/or assists in the bonding of the decorated print layer to the durable coating film 6 (such as an automotive-grade PU or PU/acrylate hybrid or fluoropolymer hardcoat layer) which would be in contact with the bottom mold surface 205, IMD: in-mold decoration layers of the TIMFF, and IMC: in-mold coating layers of the TIMFF. The IMD layers had been cured mainly during the exothermic heat cycle of Stage 1 while the IMC layers are cured mainly during the platen heat cycle of Stage 2. More specifically, the bottom mold 205 is heated by a platen heater attached to it. This heat activates the reactive PU bonding resin layer 5 and accelerates the curing of the PU or PU/acrylate hybrid or fluoropolymer hardcoat layer 6. The platen and

The manufacturing process of the invention, described in detail above by considering a class of non-limiting exemplary embodiments, enables the fabrication of simultaneously in-mold decorated and in-mold coated thermoset articles, greatly reducing the secondary finishing costs.

D.1. Introduction

D.2. Use of Biobased Feedstocks

A manufacturer that knows what percentage of each ingredient in the formulation of its product originated from a biobased source (as indicated by the supplier of each formulation ingredient) can use this information to calculate theoretical biobased content for the product.

If at least 10% of the article resin that the mold fills with is derived from biobased feedstocks, the manufacturing process will henceforth be referred to as Custom Bio-Composite--Reaction Injection Molding (CBC-RIM). (The qualifier "Custom" highlights the fact that the formulations used in implementing the process of the invention can be customized to meet the requirements of many different applications.) On the other hand, if the biobased content of the article resin that the mold fills with is less than 10%, then the manufacturing process will be referred to as Custom Composite--Reaction Injection Molding (CC-RIM). If the article resin contains reinforcements, then these processes will instead be referred to as Custom Bio-Composite--Reinforced Reaction Injection Molding (CBC-RRIM) and Custom Composite--Reinforced Reaction Injection Molding (CC-RRIM) respectively. The biobased content of the article resin that the mold fills with is at least 40% in some other embodiments and at least 70% in yet some other embodiments.

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D.3. Use of Feedstocks Originating from Recycled Polymer Wastes

Recycled polymer wastes may comprise polymer manufacturing process wastes, post-consumer polymer wastes, and mixtures thereof, which would otherwise probably have gone to a landfill or an incinerator. As non-limiting examples, processes exist for the chemical depolymerization of products such as post-consumer PET bottles and PU foams into oligomers which can then be converted into PU precursors (such as polyols).

E. Manufacturing Process Production Flow

While roll lamination is a possible sub-process that helps in handling the film in some implementations of the invention, some other implementations comprise extrusion of B-stage film or sheets on a mold followed by setting the entire mold and film into a printer and then moving them again for molding as the final process step. In such implementations, the textured mold acts as a chiller for the molten TIMFF before printing. This approach is often advantageous for molding parts that are thicker than 3 millimeters. The molding process can be any of reaction injection molding, injection molding, compression molding, resin transfer molding, spin casting, rotational molding, thermoforming, roll lamination, use of a platen/laminate press, and blow molding in implementations manufactured in this manner. As a non-limiting example, compression molding may be advantageously performed for articles of thickness below 3 mm where a liner-supported TIMFF is combined with a pre-preg (reinforced or structural), and then cured with heat and pressure in a platen press for lamination or in a compression mold press, to become a part of an article such as but not limited to an engine shroud, hood, body panel, tile, or decorative part.

FIGS. 13A-13B compare some details of embodiments using direct extrusion to a texture plate and embodiments using a roller.

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F. Applications

The applications of the TIMFF technology include, but are not limited to, the following:

(4) Applications in the transportation industry, including but not limited to uses in vehicles; as in aerospace,

(b) "Laminate Flooring Sustainability Standard", NALFA (North American Laminate Flooring Association) Standards Publication LF 02-2011 (2011). This voluntary standard provides measurable market-based definitions of sustainable laminate flooring by establishing performance criteria that address environmental and social aspects throughout the supply chain. Its intent is to encourage reduction in environmental impact. It addresses sustainability in four major areas and provides a scoring system: (Section 5) Product design, to encourage integration of environmental and life-cycle thinking into the product design process. (Section 6) Product manufacturing, to encourage the quantification of environmental impacts from manufacturing and production and the taking of action to reduce these impacts. (Section 7) Durability and use, to encourage production of durable (long-lasting) products which are environmentally friendly during use. (Section 8) Social responsibility and progressive corporate governance, to encourage good business practices and continued social responsibility. The maximum number of points attainable by meeting all of the sustainability criteria described in these four sections of the standard is 98. In addition (Section 9), a manufacturer can gain up to ten points by demonstrating innovations in the product design, development, and/or manufacturing process, so that the maximum number of points attainable by a product that meets all of the sustainability criteria in addition to manifesting significant innovation is 108. The criteria used in calculating the overall sustainability score of a product and the number of points assigned to each criterion are listed in Annex A of NALFA Standards Publication LF 02-2011 (2011). In developing preferred embodiments of the invention intended for use as molded flooring products, among embodiments of similar cost that meet the performance criteria listed in Table 2-1 of NALFA Standards Publication LF 01-2011 (2011) and provide comparable levels of performance, an embodiment that has a higher sustainability score according to the scoring system detailed in Annex A of NALFA Standards Publication LF 02-2011 (2011) will be preferred over an embodiment that has a lower sustainability score.

(d) The NSF/ANSI 332 certification process is based on NSF 332-2012, "Sustainability Assessment for Resilient Floor Coverings" (31 Oct. 2012, NSF International). It was developed by the NSF National Center for Sustainability Standards (NCSS) in collaboration with the American National Standards Institute (ANSI). It is recommended by the Resilient Floor Covering Institute (an industry trade association). It is performed by NSF/NCSS. Sustainability is assessed quantitatively in six areas (product design, product manufacturing, long-term value, end-of-life-management, corporate governance, and innovation) and points are assigned. Total points earned determine certification at the Conformant, Silver, Gold, or Platinum level. Optionally, some embodiments of the invention will be able to earn certification at least at the Conformant level in the NSF/ANSI 332 certification process if such certification is sought.

As of the date of this disclosure, we are not aware of industry standards that have been developed specifically for graphic panels for structural signage and structural graphics. We anticipate, however, that NALFA Standards Publication LF 01-2011 (2011) and NALFA Standards Publication LF 02-2011 (2011), which were developed for molded laminate flooring products, will also be helpful in selecting preferred

embodiments of the invention for use as graphic panels for durable signage and structural graphics. As a non-limiting example, Table 2 illustrates how NALFA Standards Publication LF 01-2011 (2011) and some other standard tests may be used in different ways for graphic panel applications as compared with flooring applications in selecting embodiments of the invention possessing attractive performance characteristics relevant to the intended application.

TABLE-US-00002 TABLE 2 A non-limiting illustration of how NALFA Standards Publication LF 01-2011 (2011) and some other standard tests may be used in different ways for graphic panel applications as compared with flooring applications in selecting embodiments of the invention possessing attractive performance characteristics relevant to the intended application. Desirable Property Measurement Method Essential Performance Properties described Static load, Thickness Must pass all 11 tests for The higher the in the NALFA swell, Light resistance, flooring applications. better, both to Standards Cleanability/Stain The testing needs differ for provide a larger Publication LF 01- resistance, Large ball outdoors graphic panel safety margin 2011 impact resistance, applications: and to have a Small ball impact The static load, light product that may resistance, Wear resistance, and Castor be useful in a resistance, Dimensional chair resistance tests will broader range of tolerance, Castor chair not need to be applications resistance, Surface performed. Bond, Formaldehyde The NALFA light resistance test is replaced by one or more of ASTM D1435, ASTM D4141, and/or ASTM D4364. The NALFA cleanability/stain resistance test lists 15 household substances, among which only six are relevant for an outdoors graphic panel: Distilled water, 10% citric acid, black permanent marker, # 2 pencil, wax crayon, and black paste shoe polish. The following NALFA tests will still be needed: Thickness swell, large ball impact resistance, small ball impact resistance, wear resistance, formaldehyde. Optional but useful for quality assurance: dimensional tolerance, surface bond. Weatherability ASTM D1435, ASTM 10 year outdoor life The higher (mainly for outdoor D4141, and/or ASTM performance the graphic panel D4364 better in products, but also accelerated for flooring weathering tests, products targeted both to provide a for outdoor use) larger safety margin and to have a product that may be useful in a broader range of applications Graffiti resistance NALFA Easy to clean Never needs cleanability/stain cleaning resistance tests with six substances (distilled water, 10% citric acid, black permanent marker, # 2 pencil, wax crayon, and black paste shoe polish) will be useful. ASTM D6578 (Standard Practice for Determination of Graffiti Resistance) may be used as an additional and/or alternative test.

In the fields of aerospace and automotive structures and body panels, non-limiting examples of industry standards include sets of standards that are recommended by the Society of Automotive Engineers (SAE International) and can be found and purchased on its website.

American Society for Testing and Materials (ASTM International) and the International Organization for Standardization (ISO) are additional non-limiting examples of organizations that have published industry standards some of which may be relevant to defining the performance requirements of products manufactured according to the invention. For example, ASTM D4762-11a, "Standard Guide for Testing Polymer Matrix Composite Materials" (1 Aug. 2011), summarizes the application of ASTM standard test methods (and other supporting standards) to continuous-fiber reinforced polymer matrix composite materials and is incorporated herein in its entirety by reference.

Some Envisioned Applications of TIMFF

With the benefit of this disclosure, it is possible for a worker of ordinary skill in the field of the invention to design customized versions of TIMFF in many different formats for an almost unlimited range of applications where a need exists to decorate and/or enhance the durability of a fabricated article. For example, a TIMFF may be formulated as an exterior, interior, sign, and/or structural grade; and it may be (a) extruded or cast as an integrated part of an inline production process, (b) produced as a durable clear and opaque white resin cast film on a liner or carrier sheet and supplied in rolls, (c) extruded or cast as an unsupported film or sheet (defined as a film if the thickness does not exceed 10 mils and as a sheet if the thickness is greater than 10 mils) and cooled to B stage and stored as flat sheets or roll stock, or (d) pre-printed as a woven or non-woven prep-preg containing synthetic or/and natural fibers and cooled or partially cured to B stage. Some non-limiting envisioned applications of the many customized TIMFF products that can be designed in various formats as exterior, interior, sign, and/or structural grades are detailed further below to facilitate the teaching of the invention.

Advantage over paint: Coil steel supplied to forming company finished with AATFF ready to form and weld--No painting step--Superior, UV, scratch, shine, etc.--Can be customized with images, fades, metallic, pearlescent etc. Film application and molding method: Platen press or UV lamination then molded by compression molding

Decor Layer: 1. Automotive paint Mica (pearlescent) additive Aluminum (metallic) additive 2. Primer layer (paint-receptive) 3. Reactive (coil steel or carbon composite-receptive) layer B. Bio-Composite Flooring--Thermoset Finishing Film (BCF-TFF) Advantage over High Pressure Laminate: Less time and cost to produce--no post mounting and routing--Biobased resin--no VOCs, formaldehyde--can be used in wet environment--better UV, scratch resistance, less shrinkage Molding method: RIM--easy lock mold shape--textures and in register textures

Decor Layer: 1. Print 2. PU with alumina trihydrate additive-primer layer (print-receptive) Mold Resin-PU (RIM PU with filler for quiet flooring) layer C. Exterior Graphic Lamination--Thermoset Finishing Film (EGL-TFF) With this film digital print and sign companies can print to the film and mount it to a specific substrate with our method. The result will be an exterior grade graphic panel that will be vandal and graffiti resistant and not fade more than 20% over a 10 year outdoor exposure.

Decor Layer: 1. Print 2. Clear print primer layer (print-receptive) 3. Reactive (filler-receptive RIM PU-acrylic hybrid resin) layer D. Interior Wall Tile--Thermoset Finishing Film (IWT-TFF) Advantages over other types of wall tiles: Custom images and textures, less energy, cheaper to produce, etc.

Decor Layer: 1. Print 2. Primer layer (print-receptive) 3. Reactive (RIM PU receptive to talc and/or alumina trihydrate filler) layer E. Kitchen/Bath/Floor Tile--Thermoset Finishing Film (KBFT-TFF) Advantage over other types of KBF wall tiles: Custom images and textures, less energy, more scratch resistance, higher break point, cheaper to produce, etc.

Decor Layer: 1. Print 2. Primer layer (print-receptive) 3. Reactive (RIM PU receptive to talc and/or alumina trihydrate filler) layer F. Solid Surface--Thermoset Finishing Film (SS-TFF) Advantage over other types of wall tiles: Custom images and textures (not available today with other solid surface products), addition surface protection, cheaper to produce, etc. Casting method: Open pour methods

Decor Layer: 1. Print G. Vacuum/Thermoforming--Thermoset Finishing Film (VT-TFF) Thermoformed backlit signs--Decorative components (toys, auto etc.) Advantage: One process replaces multiple steps, can add textures, superior backlit quality, less time and expense to produce, etc.

Decor Layer: 1. Print 2. Clear print primer layer (print-receptive) 3. Polycarbonate thermoplastic receptive

Example 1: Solvent-Mixed and Cast B-Stage PU Films

The solvent manufacturing approach offers the advantages of easy and rapid formulation preparation. Furthermore, different ways are available to coat solvent-based formulas. Hence solvents were used to prepare and test a large number of possible formulations in a relatively short period of time. Thus the development of B-stage polyurethane films via solvent mixing and casting was explored thoroughly within the design space defined by a specific non-limiting set of formulations to identify a promising formulation within this design space. It should be emphasized that this is only one of the many possible promising formulations, being used as an example for purposes of illustration, within this design space. Furthermore, many other non-limiting promising formulations may be identified by using similar experimental procedures but starting from different sets of formulation ingredients.

A major requirement for many TIMFF applications is excellent weatherability. TIMFFs developed by using PU formulations prepared from polycarbonate diol and aliphatic isocyanate raw materials are expected to manifest excellent weatherability. Hence such formulations were explored in this set of experiments, with the following formulation ingredients: MEK solvent (methyl ethyl ketone); boiling point=80.degree. C.; <300 ppm H.sub.2O THF solvent (tetrahydrofuran); boiling point=65.degree. C. UH50 (linear) polycarbonate diol; --OH equivalent weight=224 mg KOH/g UH50, UBE America Inc. UM90 (3/1 cyclic/linear) polycarbonate diol; --OH equivalent weight=224 mg KOH/g UH50, UBE America Inc. UH200 (linear) polycarbonate diol; --OH equivalent weight=56 mg KOH/g UH200, UBE America Inc. Desmodur PL340 blocked IPDI isocyanate; equivalent weight as supplied=958 g/mol; activation temp=130.degree. C.; Bayer Material Science Desmodur BL3475 blocked HDI+IPDI isocyanate; equivalent weight as supplied=680 g/mol; activation temp=121.degree. C.; Bayer Material Science Desmodur BL3370 blocked HDI isocyanate; equivalent weight as supplied=674 g/mol; activation temp=120.degree. C.; Bayer Material Science Vestagon EP-BF 1350 polyisocyanate adduct; equivalent weight as supplied=325 g/mol; activation temp=160.degree. C.; Evonik Vestagon EP-BF 9030 polyisocyanate adduct; equivalent weight as supplied=350 g/mol; activation temp=120.degree. C.; Evonik Trixene BL 7951 blocked IPDI trimer, equivalent weight as supplied=539 g/mol; activation temp=.about.120.degree. C.; Chemtura/Baxenden Chem. LTD. Dabco T-12; dibutyltin dilaurate catalyst; Air Products Inc. BiCat 8; 50/50 zinc-bismuth catalyst; Shepherd Chemical Co. BiCat Z; zinc catalyst; Shepherd Chemical Co. Incozol 2; moisture scavenger; Incorez Inc. Used as drying agent. Di-TMP; di(trimethylolpropane); crosslinker; Perstorp Corp. Chroma-Chem UCD 1106V white pigment; Chromaflo Technologies Inc. Litho 105 C2S paper casting sheet; Burkhardt/Freeman, Inc. Sample Preparation Mixing: Each PU formulation was prepared as two separate parts A and B, and then poured together in a jar and rolled for 1 hour prior to casting films. Part A consisted of UM50, UM200 or UM90 (3:1) polycarbonate diol, MEK solvent, catalyst, drying agent, and whitener, if any. Diols were heated to 65.degree. C. to be able to pour them from their canisters. Catalyst, drying agent, and MEK solvent were added to the still warm diol and the mixture was rolled overnight to achieve complete dissolution of the polyol. A crosslinker, di-TMP was added to some Parts A. In order to achieve solubilization of di-TMP in Part A, it was necessary to melt the required amount into 115.degree. C. molten polycarbonate diol. After the di-TMP was dissolved, the other Part A components were then added. Part B consisted of isocyanate and MEK and THF solvents. The isocyanate and solvents were added together and rolled in a jar overnight to achieve complete dissolution. Coating: A Mayer rod #100 was used on a ChemInstruments drawdown coater to cast thin (4-5 mils dry thickness) urethanes onto casting paper, UV-ink printed paper and Bemis thermoplastic urethane (white or printed). A ChemInstruments LC-100 bull nose coater with 30 mil shims between the coater rolls was used to cast thick (10-20 mils dry thickness) PU formulas. Sample Drying: Samples Were Dried Slowly in Stages: (1) Thick, free-film PU sheets were dried 60 minutes on lab bench at room temperature followed by 10 minutes at 50.degree. C. in a circulating air oven. These very mild drying conditions were necessary to end up with a film of sufficient thickness that is still flexible enough to be manually manipulated a sheet. (2) Drying stages applied to thin PU coatings on printed and unprinted Bemis films and on UV-ink printed paper were: 20 minutes at room temperature, 20 minutes at 60.degree. C. and finally, 15 minutes at 75.degree. C. Sample Curing:

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The testing program summarized below was implemented for the rapid initial screening of many formulations prepared by using the ingredients listed above. This testing program consists of techniques used to discriminate rapidly between better and worse formulations in the formulation development stage of the project. Additional (more quantitative) tests, familiar to workers in the field of the invention, can be used to characterize the formulations as well as the dried but uncured and the cured films obtained from the formulations, and will be useful in future work focusing on formulation development but were not needed for preliminary screening. Hardness and elasticity were determined visually under 20.times. magnification by poking, pulling and scraping on a sample with sharp stainless steel tip. Clarity and yellowness were determined visually. Coefficient of expansion upon curing of a PU film was measured by marking a length on a dried but uncured film, curing the film and then re-measuring the marked length. Percentage of retained solvent was measured by weighing an aluminum dish containing undried PU and then re-weighed following various drying stages. Solvent PU formula viscosities were judged by experience to fall between 200 and 500 centipoise (at room temperature). Identification of an Exemplary Promising Formulation Within Design Space

Many formulations were prepared by using the ingredients listed above and subjected to the testing program summarized above for the rapid screening of initial formulations.

After some preliminary experiments, UBE's UM-90 polyol, which has the consistency of taffy at room temperature and hence had to be heated up to the range of 60 to 65.degree. C. to become pourable, was selected from among the tested polycarbonate diols for use in further experiments.

After some preliminary experiments, Evonik's EP-BF 9030 polyisocyanate, which has an adduct structure wherein a single molecule has two isocyanate groups that react at lower temperature and two isocyanate groups that react at elevated temperature, was selected from among the tested isocyanates for use in further experiments.

After some preliminary experiments, Dabco T-12 was selected from among the tested catalysts for use in further experiments.

The crosslinker di-TMP created difficulties in processing without providing a significant further improvement in the cured film strength and hardness. Hence it was not included in the identified exemplary promising formulation.

The Incozol 2 drying agent (moisture scavenger), which reduces the amount of water in the reactive system and thus also reduces reactions between water and isocyanates, was found to be useful in reducing the frequency of bubbles on the dried and cured PU films.

Only the UCD 1106V white pigment was used in this series of preliminary screening experiments. Further improvements in PU film properties may be envisioned to result from the consideration of alternative pigments in future work.

The use of MEK as the sole solvent was sufficient for Part A of the formulation. On the other hand, a mixture of MEK and THF was needed for Part B because the EP-BF 9030 isocyanate did not dissolve in pure MEK.

The formulation listed in Table 3, which was cast on Burkhardt/Freeman casting paper grade Litho 105 C2S, is a promising non-limiting exemplary formulation identified from among the tested formulations.

TABLE-US-00003 TABLE 3 An exemplary promising solvent mixed and cast B-stage PU formulation identified within a design space comprising polycarbonate diol and aliphatic isocyanate raw materials. The isocyanate:polyol crosslinking ratio {NCO:OH} is 1.24 to 1 in the formulation shown below. Part

Component	Grams
Part A UM90 polyol	30
MEK solvent	30
Dabco T-12 catalyst	0.95
Incozol 2 drying agent	1.9
UCD 1106V white pigment	2.58
Part B EP-BF 9030 isocyanate	65.17
MEK solvent	43.45
THF solvent	21.72

After the preparation of Part A and Part B, the final mixing step consists of adding Part A to Part B

and agitating (via rolling or stirring) for 60 minutes.

Example 2: Extrusion-Mixed and Cast B-Stage PU Films

This example involves switching from the solvent mixing and casting of B-stage PU films to solvent-free mixing and casting via extrusion. While the solvent manufacturing approach offers the advantages of easy and rapid formulation preparation, the extrusion manufacturing approach offers some other advantages; namely, (a) easier manufacturing of defect-free films (since no solvent is used so that there is no risk of formation of defects such as bubbles of solvent trapped in the film), (b) avoidance of the economic as well as environmental costs of the use of chemicals (solvents) which don't end up in the manufactured product, and (c) the ability to use a broader range of casting sheets that can be wetted uniformly by the uncured PU formulation. Hence both the solvent manufacturing and the extrusion manufacturing approaches are useful in practice and each approach is more beneficial to use than the other under different circumstances.

The initial formulation used in the extrusion manufacturing trials differs from the solvent manufacturing formulation shown in Table 3 by the omission of the two solvents (MEK and THF) as well as the omission of the whitener UCD 1106V.

The following are non-limiting examples of the design variables to be evaluated during the extrusion manufacturing trials: Variation of NCO:OH feed rate ratio on the extruder from 1.1:1.0 up to 1.5:1.0. Evaluating neopentyl glycol at 1%, 3% and 5% by weight (based on total weight of polyol and isocyanate) as a reactive formulation ingredient. Substituting BiCat 8 for Dabco T-12 catalyst to determine whether doing so can lower the temperature needed for in-mold or for post-mold curing. Testing the use of pure dry TiO₂ as a white pigment. Varying the amount of Incozol 2. Evaluating the use of alternative casting papers.

The material flow through the melt mixing process may follow the following sequence of steps in some non-limiting embodiments of the extrusion manufacturing process:

- (1) Feeding of molten UM90 into the barrel of an extruder running at a temperature in the range of 60.degree. C. to 85.degree. C. by a heated platen remelter.
- (2) Addition of EP-BF 9030 isocyanate flakes to the extruder by a solids feeder, with material temperatures preferably remaining below 100.degree. C. and the material remaining in the isocyanate mixing portion of the barrel for less than 10 minutes. If the mixing is intense, the extruder operator may use the extruder's hot oil system to cool the mixing barrel to <100.degree. C.
- (3) Catalyst, drying agent, and whitener (if any) are added to the extruder via small feed rate ports.
- (4) The uniform melted mixture then feeds a melt gear pump leading directly to a slot coating die or the melted mixture fills pails or drums for transport to a coating facility.

FIGS. 14A-14C show the details of one possible equipment layout that may be used in manufacturing embodiments of the invention by the method described in Example 2. (This non-limiting example includes the incorporation of an optional additive that renders the printable resin white and opaque in the fragment of the drawing labeled as "White Option" while this additive is not used and thus the printable resin is clear in some other non-limiting examples.) Most of the notation has been introduced in FIGS. 1, 12, and 13. The following additional notation is used: 407: B-stage TIMFF applied to release liner, 408: B-stage TIMFF with release liner, 501: TIMFF resin (print and release liner optional), 502: structural or reinforced pre-preg (B-stage roll stock), 503: TIMFF white option (print and release liner optional), 504: combined layers, 505: laminating rollers, 506: pull rollers, 507: cut and stacked finished custom laminate, 508: top mold, 509: texture plate, 510: bottom mold, 511: frame of platen press, and 512: laminate sheet cutter.

FIGS. 15A-15C show the details of another possible equipment layout that may be used in manufacturing embodiments of the invention by the method described in Example 2 while FIGS. 16A-16B illustrate a completed in-mold coated and in-mold decorated article that may be manufactured by using the equipment layout shown in FIGS. 15A-15C. Most of the notation used in these drawings has been introduced in the context of the earlier drawings. The only new notation is 701: TIMFF extrusion molding die. The method

illustrated in FIGS. 15A-15C combines decorating and coating extruded articles by adding an extrusion mold and running the TIMFF through the mold (or die) at the same time the product is extruded. Decorative extrusions including framing material, furniture edging and many others can be made by using this fabrication method. In FIG. 16B, the completed article is shown from a perspective where the TIMFF (combined IMD/IMC) placed on the article can be clearly seen.

FIGS. 17A-17C show some of the details of yet another possible equipment layout that may be used in manufacturing embodiments of the invention by the method described in Example 2 while FIGS. 18A-18C show further details of the manufacturing of embodiments of the invention according to the method illustrated in FIGS. 17A-17C. A completed in-mold coated and in-mold decorated article that may be manufactured by using this method is illustrated in FIG. 18C. The method of FIGS. 17A-17C and 18A-18C involves the use of spin casting using TIMFF to produce custom decorated or labeled pipes or tubes. The following notation is used: 801: extruded coating resin on flexible texture plate with printed and extruded white TIMFF layer, 802: TIMFF and texture plate rolled into mold, 803: spin bars hold mold to spin motor assembly, 804: tube/pipe mold, 806: spin molding chamber, 807: motor assembly, 808: mold cap and resin feed line, 809: demold graphic tube/pipe, and 810: tube or pipe complete with TIMFF (IMD/IMC. Not only will these products be decorated and coated but they can be texturized at the same time. In one particular embodiment, the TIMFF resin is extruded onto a flexible texture plate (possibly silicone rubber attached to a flexible mold plate). The flat resin-coated texture plate is then printed, white film is applied to it, and then it is bent around to form a cylinder mold. This cylinder mold is capped and then mounted onto the motor assembly. Reinforced resin is injected during the spin casting process. The mold continues to spin until the reactive resin cures. The final completed decorated and coated tube or pipe can then be removed from the mold.

The present disclosure may be embodied in other specific forms without departing from the spirit or essential attributes of the invention. Accordingly, reference should be made to the appended claims, rather than the foregoing specification, as indicating the scope of the disclosure. Although the foregoing description is directed to the preferred embodiments of the disclosure, it is noted that other variations and modification will be apparent to those skilled in the art, and may be made without departing from the spirit or scope of the disclosure.

