
(12) **UK Patent Application** (19) **GB** (11) **2 080 315 A**

(21) Application No **8023983**
(22) Date of filing **22 Jul 1980**
(43) Application published
3 Feb 1982

(51) **INT CL³**
C08L 67/06 (C08L 67/06
1/10)

(52) Domestic classification
C3M 109 163 XC

(56) Documents cited

GB 1476591
GB 1472367
GB 1442790
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GB 1424488
GB 1409950
GB 1401899

US Reissue 29915A

(58) Field of search

C3M
C3V

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(54) **Unsaturated polyester resin compositions**

(57) A polyester resin composition for a pultrusion process comprises a homogeneous mixture of (A) a polyester resin which has a Barcol hardness of not less than 45 and which is formed from (a) a polyester made by the condensation of one or more dicarboxylic acids and/or anhydrides, of which at least 60 mole percent are alpha, beta-unsaturated

dicarboxylic acids and/or anhydrides, and one or more dihydric and/or polyhydric alcohols, and (b) a monomer or mixture of monomers copolymerizable with the polyester, and (B) a minor amount of a cellulose ester resin that is soluble in the polyester resin. The preferred cellulose ester resin is cellulose acetate butyrate having an average butyrate content of at least 44 weight percent, used in amounts up to 10 percent by weight of the composition.

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SPECIFICATION

Improvements in or relating to polyester resin compositions

This invention relates to polyester resin compositions and to a process for producing reinforced polyester resin products employing a pultrusion process.

5 Pultrusion is a relatively new process for producing reinforced plastics products. Generally, the term "pultrusion" is used to describe any process for producing reinforced plastics products in which continuous reinforcing material is impregnated with resin and pulled through a die of desired cross section to shape and cure the resin and produce continuous lengths of cured product having a uniform cross section and the shape of the die. Thermosetting resins are used almost exclusively at the present 10 time with polyester resins comprising up to about 90 percent of the total and epoxy resins the rest. 10

In a pultrusion process, the reinforcing material can be any filamentary material having strength, for example glass fibre, Aramid fibres, boron fibres or graphite fibres, but customarily, E-glass fibres constitute the most commonly used reinforcing material. Filamentary reinforcing materials can be used in the form of rovings, tows, mats or cloth, or in any combination of these forms.

15 Because a pultrusion process incorporates continuous strands of reinforcing material, it produces a product much stronger and flexible than those produced by older extrusion processes, which can only utilize discontinuous lengths of reinforcing filamentary material. Because of these characteristics, whenever there are desired high-strength products having the customary properties of polyester resins, such as corrosion resistance, electrical resistance or lightweight, then pultrusion will be used. The sizes 20 and shapes of products, either solid or hollow, which can be produced by pultrusion is virtually unlimited, as for example I-beams, channel, wide-flange beams, solid bars and rods, round and square tubing, rectangular beams, angles, and even flat sheets. Customarily, the thickness of these parts can range from as little as 1/8 inch up to a practical maximum of about three inches.

Initially, pultrusion was costly and was limited to the manufacture of products with small cross-sectional areas. During the 1950's, however, radio frequency (RF) preheating was developed, which 25 permitted faster line speeds and larger cross-sectional products to be made. However, even with RF-augmented heating, there is a practical limit to pultrusion speed beyond which pultruded parts exhibit either internal thermocracking due to excessive exotherm, or external or internal cracking due to undercuring and monomer gassing. Typically, products having a thickness ranging from about 0.25 to 30 about 0.375 inch made with relatively fast-curing polyester resins can be pultruded at speeds up to about 9 feet per minute with fairly smooth surfaces; products having a thickness ranging from about 0.375 to about 0.675 inch made with an intermediate reactivity resin can be pultruded at speeds up to about 6 feet per minute with only mildly abraded surfaces; while products over 0.675 inches in 35 thickness and made with medium reactivity resins are limited to speeds of up to about 5 feet per minute (and may be as low as 0.5 feet per minute depending on thickness) and have pronounced surface abrasion and roughness. Additionally, because of the thermal cracking that occurs when the curing exotherm is excessive, thick parts generally can only be made with medium reactivity resins having a maximum degree of unsaturation of about 50 to 55 mole percent of the total diacids (100 mole percent) employed in producing the resin. Because of their limited reactivity, these resins tend to give softer 40 cured surfaces that are more prone to be abraded in the die and to give products having rough, uneven surfaces. 40

According to one aspect of the present invention there is provided a polyester resin composition comprising a homogenous mixture of (A) a polyester resin having a Barcol hardness not less than about 45 and formed from a polyester made by the condensation of an alpha, beta-unsaturated diacid or 45 anhydride and a dihydric or polyhydric alcohol, and a monomer or mixture of monomers copolymerizable with the polyester, and (B) a minor amount of a cellulose ester resin that is soluble in the polyester resin and causes the mixture when cured to be opaque. 45

According to another aspect of the present invention there is provided a process for producing a reinforced polyester resin product with process comprises pultruding a polyester resin composition 50 according to the present invention. 50

The polyester resin compositions of the invention can be pultruded at greater speeds to give products having diminished surface roughness and internal and/or external cracking. Additionally, certain of the polyester resin compositions according to the invention have been found to give bulk or sheet molding compositions capable of producing thick moldings that are crack-free.

55 In the following description all parts, phr (parts per hundred of resin), and percentages are calculated and expressed on a weight basis. 55

The polyesters employed in the polyester resin compositions of the invention are the condensation products of one or more dicarboxylic acids and/or anhydrides (100 moles %) with a slight excess of one or more dihydric or polyhydric alcohols (about 105—110 mole %), chosen to provide a polyester which, 60 when combined with a copolymerizable monomer, as hereinafter described, and cured, form a polyester resin having a Barcol hardness of about 45 or greater, as determined by ASTM test method, D 2583—75 employing a 0.125 inch-thick cured clear casting. For the polyester to provide a polyester resin with this hardness and the reactivity necessary for the process of the invention, it is believed that at least about 60 mole percent of the total dicarboxylic acids (and/or anhydrides) used to make the resin 60

should be of the alpha, beta-unsaturated type, copolymerizable with the monomers. In some instances, when high reactivity is desired, as for example when the polyester resin is to be utilized with a large quantity of the cellulose ester resin, 90—100 mole percent of the dicarboxylic acids employed will be alpha, beta-unsaturated. More typical, however, are polyesters made with about 65—85 mole percent unsaturation, with about 75—80 mole percent being optimum. Examples of alpha, beta-unsaturated acids that can be employed to provide this unsaturation are maleic, fumaric, chlorameleic, itaconic, and like acids and/or their anhydrides. The balance of any diacids or anhydrides employed to modify the reactivity and properties of the polyester may be either saturated or of the non-alpha, beta-unsaturated type, and may be, for example, phthalic, isophthalic, tetrahydrophthalic or tetrachlorophthalic acid, hexachloroendomethylenetetrahydrophthalic acid or low-molecular-weight aliphatic dicarboxylic acids, such as succinic, adipic or diglycolic acid, or their anhydrides. As previously described, the degree of alpha, beta-unsaturation and, hence, reactivity of the polyester and the modifying diacids should be chosen so as to give a polyester resin having the desired Barcol hardness. In this connection, it is known that the aliphatic diacids tend to impart softness and, therefore, must be used in minor amounts. Conversely, it is known that the aromatic diacids, such as the phthalic or the halophthalic acids, impart hardness and can be used in larger quantities. When fire retardancy is desired, a halogenated diacid, such as tetrachlorophthalic acid or its anhydride is used, or a non-alpha, beta-unsaturated acid, such as tetrahydrophthalic acid is used and then halogenated after condensation. Examples of suitable dihydric or polyhydric alcohols that may be used are glycols, such as ethylene glycol, propylene glycol, 1,4-butane diol, neopentyl glycol, 2,2-bis-(4-hydroxycyclohexyl)propane and the adduct of two moles of propylene oxide with bisphenol A. Polyether glycols, such as diethylene glycol and dipropylene glycol also may be utilized but only in small quantities, because of their softening effect on the polyester after cure. Similarly, it may be necessary to limit the quantity of ethylene glycol in the polyester when the resin is to be dissolved in large quantities of monomer, as for example 55 to 60 percent monomer, since ethylene glycol lowers the monomer solubility of the polyester.

The molecular weight of the polyester is not narrowly critical and varies typically between about 1500 and about 3500 with an acid number ranging from about 20 to about 35.

There may be used in the polyester resin compositions of the invention either a single polyester or a mixture of two or more polyesters such that, after mixing, the combined total of the diacids and glycols present in each will give a final polyester resin system having the desired Barcol hardness and reactivity. An example of such a mixture is shown in Example 1. Generally, such mixtures have the same physical properties as a single polyester made with the same total quantity and types of condensation reactants used to make the two separate polyesters.

Polyesters giving especially high pultrusion speeds and pultruded products with minimal or no surface abrading or internal or external cracks, and hence constituting one of the preferred embodiments of the pultrusion polyester resins of this invention, are those having a styrene compatibility of about 25% or less and an alpha, beta-unsaturation (—C=C—) equivalent weight of about 200 to 275. Such polyesters are typically made by the condensation of about 65 to about 85 mole percent of a suitable alpha, beta-unsaturated diacid (usually maleic acid) and 15—35 mole percent of a suitable modifying diacid, with a slight excess (e.g. 105—110 mole percent) of suitable glycol(s) — the condensation reactants being chosen to provide the polyester with this degree of styrene compatibility. A definition and method of determining "styrene compatibility" is given in U.S. Patent Specification No. 3,940,350, column 4, lines 3—50.

In addition, polyester resin compositions made with polyesters having this degree of styrene compatibility and (—C=C—) equivalent weight have been discovered to give bulk and sheet molding compounds capable of being molded in thick sections (0.67 inch and greater) without cracking.

The monomers used in forming the polyester resin are, most preferably, styrene or vinyl toluene or mixtures of the two employed in a quantity of about 40 to 55 weight percent of the total weight of the polyester resin. In certain instances, as little as 40 percent or as much as 60 percent monomer may be employed. However, when less than about 45 percent monomer is used, it may be necessary to use as the cellulose ester resin a low-molecular-weight cellulose acetate butyrate, such as EAB 551—0.01, to obtain an acceptably low resin viscosity. Alternatively, such low-monomer content polyester resins may be heated in the impregnation tank to reduce viscosity to an acceptable level. This, of course, may require using catalysts having higher activation temperatures to prevent premature gellation. Conversely, more than about 55 percent monomer is usually only employed when physical properties are not especially critical and lower cost is paramount. Typically, physical properties are maintained at high levels up to about 55 percent, at which point they start to drop.

Generally, the quantity of monomer employed is determined by the viscosity requirement of the intended pultrusion process, taking into consideration the type and molecular weight of the polyester and cellulose ester resin being employed in the system-viscosity decreasing with increasing monomer. In this connection, when the pultrusion composition is to be used for impregnating roving or tows, viscosities in the range of 800 to 1500 centipoises (cps) may be employed, with viscosities of 900 to 1000 cps generally being preferred. With mat or fabric reinforcement, typical viscosities are of the order of about 1500 to 2000 cps. Bearing in mind that the impregnating polyester resin formulation can be compounded with varying amounts of filler, it can be appreciated that the raw or neat polyester resin

may typically be made to have a viscosity ranging from about 500 to 2000 cps depending upon the type and quantity of filler subsequently added.

When other monomers are used to partially replace styrene and/or vinyl toluene in the polyester resin, the type and quantity chosen should be such that they give a polyester resin having a length to
 5 peak exotherm (LPE) not in excess of about 90 seconds when the resin is catalyzed with 2 percent 5
 Percadox 16 (98 percent active bis-4-t-butyl cyclohexyl peroxydicarbonate) and tested for reactivity in
 accordance with the Society of the Plastic Industry (SPI) gel-time test. When very high reactivity resins
 are desired, the LPE should not exceed about 70 seconds. Illustrative of other monomers that may be
 employed are divinyl benzene, for increased cured resin hardness; vinyl acetate for lower resin viscosity,
 10 and acrylate esters for improved light stability. Other monomers that might be considered for inclusion 10
 in the polyester resin are, for example, alpha-methylstyrene, chlorostyrene, diallphthalate, and
 triallylphosphate. In addition to providing a polyester resin having the aforescribed reactivity (LPE),
 any replacement monomers chosen should have in combination with the styrene and/or vinyl toluene an
 acceptable degree of solvating properties for the polyester.

15 A polyester resin composition of the invention will contain a minor amount of the cellulose ester 15
 resin, typically from 4 to 10 parts of a cellulose acetate butyrate resin (CAB) per 100 parts of polyester
 resin, such that it is soluble in the polyester resin to give a stable one-phase solution which, when cured
 in the neat form at a thickness of 0.125 inches, has a heterogeneous opaque appearance. CAB resins
 having these properties typically have an average butyrate content of about 0.9 to 2.0 percent. Best
 20 results have been obtained with CAB resins having a butyrate content of about 49 to 55 percent by 20
 weight. Further, to obtain polyester resin compositions that are not excessively viscous, it is preferred to
 employ CAB's having a viscosity not exceeding about 5 seconds, as determined by ASTM test method,
 D 817—65 (Formula A), and D 1343—56. Most preferred are CAB resins having a viscosity of one
 second or less. Cellulose acetate butyrate resins having these characteristics are available from Eastman
 25 Kodak under the following designations: CAB—551—0.01, —0.1, —0.1, —0.2 and —1; 25
 CAB—500—5; and CAB—451—1. If desired, mixtures of suitable CAB resins may be used. Also, there
 could be used other cellulose ester resins, such as cellulose acetate pentoate or cellulose acetate or
 cellulose acetate hexoate resinshaving the aforescribed solubility and cured-compatibility
 characteristics in the polyester resin.

30 As mentioned above, when the cellulose ester resin employed is cellulose acetate butyrate, there 30
 is typically employed from 4 to 10 parts of CAB per 100 parts of polyester resin. When less than about
 four parts of CAB resin are employed, pultruded products exhibit internal cracking and/or surface
 abrasion, while more than ten parts of CAB can give viscosities too high for satisfactory pultrusion. Too-
 high viscosities require the use of monomers in quantities greater than about 60 percent where, as
 35 previously described, physical properties are diminished. Most preferred are pultrusion polyester resins 35
 containing 5—8 phr of the CAB resin. Typically, the amount of CAB resin added is adjusted to the
 reactivity of the polyester resin being employed in the pultrusion invention compositions. For example, a
 polyester having high reactivity (i.e., one made with 95 to 100 mole percent of unsaturated acid) usually
 requires about 7 to 10 parts of CAB; a fairly high-reactivity resin (i.e., one made with about 75 mole
 40 percent of unsaturated acid), about 5 to 8 parts of CAB; a polyester of intermediate reactivity (i.e., one 40
 made with about 67 mole percent of unsaturated acid), about 5 to 6 parts of CAB; while a low-reactivity
 polyester (i.e., one made with about 60 mole percent of unsaturated acid), about 4 to 5 parts of CAB.
 Generally, the higher the unsaturated content of the polyester, the greater the cross-linking density and
 the peak exotherm temperature, and, hence, the shrinkage of the polyester upon cure. Both factors
 45 contribute to gross internal stresses, which result in internal cracking, and, hence, proportionally 45
 increasing amounts of CAB are required as the resin reactivity increases to alleviate these effects.

The polyester resin compositions utilized in the pultrusion process of the invention are easily
 prepared by dissolving the cellulose ester resin in the polyester resin, by means known to those skilled in
 the art and then adding additional monomer, if required, to give the specification viscosity desired.
 50 Alternatively, some of the monomer may be withheld from the polyester resin to predissolve the 50
 cellulose ester resin, with the resulting solution then being admixed with the polyester resin and the
 viscosity adjusted with additional monomer. If desired, solvation of the cellulose ester resin can be
 accelerated by heating the polyester resin or monomer to moderately elevated temperatures, such as
 50° to 60°C.

55 The polyester resin compositions of the invention are compounded into the final pultrusion 55
 compositions used to impregnate the reinforcing material by usual means and utilize the kinds and
 quantities of ingredients and adjuvants typically used for polyesters resins in this process.

Thus, the level of catalyst chosen is such that the polyester resin composition will be substantially
 fully cured during its residence time in the pultrusion die, and typically will be about 0.75 to 1.25 phr,
 60 with about 1 phr most commonly being employed. Preferred are catalysts having a critical temperature 60
 (or activation temperature) of about 120—145°F, such as Percadox 16 (98 percent active bis-4-t-
 butylcyclohexyl peroxydicarbonate having a critical temperature of about 120° to 122°F) or Catalyst
 USP—245 (5-dimethylhexane-2,5-diper 2-ethylhexoate having a critical temperature of about 145°F).
 Catalysts having this range of activation temperatures allow the pultrusion compound to be cured at
 65 lower temperatures which permits higher pultrusion speeds and minimizes internal thermal cracking. 65

Catalysts having higher critical temperatures, however, may at times be used to advantage with RE-augmented heating to give high pultrusion speeds, but generally are less preferred because of the necessity of heating the resin-impregnated reinforcement to a temperature within 40° to 50°F of the critical temperature of the catalyst. For example, temperatures of 100° to 120°F may be needed when
 5 benzoyl peroxide having a critical temperature of 160°F is used. At these higher temperatures, monomer vaporization increases, changing the desired ratio of polyester to monomer in the resin system. Additionally, increased monomer vapor in the air constitutes possible health and fire hazards to people working in the vicinity of the pultrusion machine. Particularly, fire caused by sparking of the radio frequency heating equipment can be a threat that must be guarded against.

10 Besides benzoyl peroxide, other catalysts having high critical temperatures, such as t-butyl perbenzoate having a critical temperature of about 200°F, may be utilized, particularly in combination with catalysts having low activation temperatures. Such combinations may be advantageous when higher running speeds are to be utilized. Generally, undercuring due to insufficient catalyst results in monomer gassing causing internal voids and/or surface hairline cracks running for various lengths
 15 through the length of the pultrusion. When observed, increasing the level of catalyst will increase the degree of cure and eliminate these defects.

The kinds and quantities of other ingredients used in the pultrusion compositions of the invention are conventional and like those used in standard pultrusion compounds. Thus, fillers, such as calcium carbonate, clay and hydrated alumina, may be utilized in quantities varying from 0 to 100 phr of the
 20 polyester resin composition, with the quantity being dictated primarily by the viscosity of the initial pultrusion polyester resin and the final viscosity required of the pultrusion composition for the intended use. Bearing this in mind, typically about 0 to 25 phr filler will be employed for tows and roving to give the desired 800—1500 cps impregnation viscosity while about 10 to 100 phr filler will be required for mat and fabric pultrusion compositions to give the desired 1500—2000 cps final viscosity. In addition
 25 to adjusting viscosity, the use of fillers also reduces cost and further lowers cure shrinkage of the pultrusion composition.

Similarly, inhibitors also are present in the invention resin compositions to prevent premature gelation of the resin during manufacture and storage and subsequently during utilization in the pultrusion process. Illustrative of useful inhibitors utilized in quantities giving the desired gel time
 30 according to standard industry practices are: hydroquinone, t-butyl catechol, and di-t-butyl-p-cresol. Other inhibitors, either individually or in combination, may alternatively be employed so long as the kinds and quantities are judiciously chosen to provide the desired SPI gel time, previously described in connection with the monomers.

Lastly, the pultrusion compositions typically utilize standard mould release agents in quantities
 35 (1—5 phr) promoting smooth extrusion and minimal die sticking. Exemplary of materials that may be used are: calcium or zinc stearate, phosphate esters or very fine (1 micron) polyethylene powder.

In the process of the invention, any type of reinforcement may be utilized that is customarily employed in standard pultrusion processes and includes filamentary reinforcements in the form of rovings, tows, mats, woven cloth and the like, either singly or in various combinations. Glass fibre
 40 constitutes the majority of reinforcement material used today and will be normally employed in the process of the invention. When special properties, such as higher strengths or lower weights, are desired, more esoteric reinforcements, such as Aramid, boron or graphite fibres may be used in any of the forms previously described. Conventionally, flat sheets are pultruded with mats or woven cloths — often reinforced with longitudinal lengths of fibre or roving — in quantities representing about 25 to 60
 45 percent of the pultruded product, with about 50 percent being most typical. When maximum adhesion between fibre reinforcement and pultrusion polyester resin is desired, chemical coupling agents are applied to the reinforcing material.

Similarly the polyester resin composition is pultruded in a manner like the polyester of the prior art except for the pulling speed which can be two to four times more rapid than the speeds used for
 50 polyesters of the prior art. Ideally, pultrusion compounds employing the polyester resin compositions of the invention are pultruded through a heated die, usually 3—5 feet long, arbitrarily divided for temperature sensing and control purposes into 4 zones. A typical die temperature profile for pultruding a compound like that used in Example 1 is shown in Table A, which shows the temperatures used as the pultruding speed is increased.

55 As can be seen from Table A, the initial set point for the control probe in Zone I should be 325°F. Zone II can go up to 340°F and Zone III to 400°F. Zone IV should be greater than 250°F before processing begins. As line speed increases and the heat from the exotherm raises the die heat, the control temperature in Zone I is incrementally lowered so as to keep Zone IV greater than 300°F, preferably 325°F. An indication of too low die heat will be the presence of internal voids. This is easily
 60 remedied by increasing the control temperature 10—20°F or lowering the radio frequency plate current so as to reduce the resin temperature 3—10°F. The speed and heat profiles shown in Table A are for R.F.-augmented-cure pultrusion equipment, but are equally applicable to thermal-only equipment, but at somewhat lower speeds.

TABLE A

Pultrusion Speed (ft/min)	Resin Temperature (°F)	Zone Die Temperatures (°F)			
		Zone I	Zone II	Zone III	Zone IV*
1	75	325-225*	325	335	315
2	90	235	320	370	315
3	95	235	320	375	335
4	100-105	240	315	375	330-345
5	105-115	265	340	400	340
6	110-115	265	335	400	335

* Control temperature is lowered from 325 to 225°F as line speed increases in order to maintain "heat profile"

The invention is illustrated by the following Examples:

EXAMPLE 1

A polyester resin was made by admixing together:

5	Polyester A	20.9%	5
	Polyester B	23.8%	
	Styrene	55.3%	
	total	100.0%	

Polyester A and polyester B and the mixture of the two comprised:

	Polyester A	Polyester B	Mixture		
maleic anhydride (moles)	0.5	1.0	0.765		
isophthalic acid (moles)	0.5		0.235		
Propylene glycol (moles)	1.05	1.11	1.085		
<u>Properties</u>					
10	styrene compatibility	10%	40%	25%	10
	LPE (2% percadox 16)			57 sec	
	(-c = c-) equivalent weight	370	160	225	
	Cured Barcol hardness	45	60	55	
	viscosity			500 cps	

A polyester resin composition was then prepared by admixing and dissolving into 100 parts of the polyester resin, 5.7 parts of Eastman Kodak's CAB—551—0.1 resin (cellulose acetate butyrate resin having about 55% butyl, 2% acetyl and 1.6% hydroxyl average content). Finally a pultrusion composition having a viscosity of 1000 cps was prepared by homogeneously admixing:

5	polyester resin composition	Parts 105.7	5
	mould release agent (phosphate ester)	1.06	
	catalyst USP—245	1.06	
	calcium carbonate filler	10.6	

This compound was used to impregnate 66-end-count glass roving that was subsequently pulled through a die producing a flat bar, 1—1/2 inch × 1/4 inch having ribbed edges, utilizing the processing conditions shown in Table 1. 10

TABLE 1

Die Temperature (°F)

Pulling Speed (ft/min)	RF Heating of Impregnated Roving	Entrance Zone	Middle Zone	Exit Zone	Comments
2.0	no	245	265	255	Good Surface, No Cracks
2.5	no	245	265	255	do do
3.0	no	245	265	255	do do
3.5	no	202	257	277	do do
4.0	no	202	257	277	do do
5.0	no	202	257	277	do do
6.0	yes	168	235	280	Some surface abrading
6.5	yes	175	235	280	Some surface abrading and cracking at corner

EXAMPLE 2

A polyester resin composition having a viscosity of 1000 cps was prepared by admixing and dissolving together first: 15

	Parts
Polyester of Example 1	47.6
Styrene	52.4
CAB—551—0.1	7.85

and then admixing into the resulting solution:

	Parts	
20	mould release agent	1.08
	catalyst USP—245	1.08

The resulting pultrusion composition was used to impregnate a 68-end-count glass roving that was pulled through the same die as used in Example 1 utilizing the processing conditions shown in Table 2.

TABLE 2
Die Temperature (°F)

Pulling Speed (ft/min)	RF Heating of Impregnated Roving	Entrance Zone	Middle Zone	Exit Zone	Comments
2.0	no	232	272	285	Good Surface, No Cracks
3.0	no	230	280	280	do do
4.0	no	230	280	280	do do
5.0	no	220	280	295	do do
6.0	yes	200	260	280	do do
7.0	yes	200	260	280	do do

5 The physical properties of the bars produced in Examples 1 and 2 are given in Table 3, which also gives the properties of a one-inch diameter pultruded bar made with 69 percent glass roving and a polyester typically used for thick-pultruded products. All property values are in pounds per square inch (psi). 5

TABLE 3

	Example 1	Example 2	Typical Prior Art
Flexural Strength	134,600	136,700	128,000
Flexural Modulus	5.6×10^6	6.1×10^6	5.3×10^6
Tensile Strength	131,200	125,700	154,000
Tensile Modulus	6.1×10^6	6.7×10^6	4.8×10^6
Compressive Strength	78,000	55,000	58,000
Compressive Modulus	5.9×10^6	6.8×10^6	3.5×10^5

10 From the data in Tables 1, 2 and 3, it is apparent that the invention pultrusion resins can be pultruded at high speeds to give products having smooth surfaces and no internal or external cracking. Additionally, the data shows that the invention polyester resins give pultruded products having superior physical properties as compared to products made with polyester resins typically employed at the present time. 10

15 In production runs at two different pultruders, a pultrusion polyester resin like that of Example 1 was used to: a) increase the pultrusion speed of a one-inch-diameter rod from 3 feet/minute to 6 feet/minute, and b) increase the pultrusion speed of a hammer handle from 8 inches/minutes to 36 inches/minute. 15

CLAIMS

1. A polyester resin composition comprising a homogeneous mixture of (A) a polyester resin which has a Barcol hardness of not less than about 45 and which is formed from (a) a polyester made by the condensation of one or more dicarboxylic acids and/or anhydrides, of which at least 60 mole percent are alpha, beta-unsaturated dicarboxylic acids and/or anhydrides, and one or more dihydric and/or polyhydric alcohols, and (b) a monomer or mixture of monomers copolymerizable with the polyester, and (B) a minor amount of a cellulose ester resin that is soluble in the polyester resin. 5
2. A polyester resin composition as claimed in claim 1, wherein from 90 to 100 mole percent of the one or more dicarboxylic acids and/or anhydrides employed in the formation of the polyester are alpha, beta-unsaturated dicarboxylic acids and/or anhydrides. 10
3. A polyester resin composition as claimed in claim 1, wherein from 65 to 85 mole percent of the one or more dicarboxylic acids and/or anhydrides employed in the formation of the polyester are alpha, beta-unsaturated dicarboxylic acids and/or anhydrides.
4. A polyester resin composition as claimed in claim 1, 2 or 3, wherein the balance, if any, of the dicarboxylic acids and/or anhydrides employed in the formation of the polyester are aromatic diacids and/or anhydrides. 15
5. A polyester resin composition as claimed in claim 1, 2 or 3, wherein up to 35 mole percent of said one or more dicarboxylic acids and/or anhydrides are saturated dicarboxylic acids and/or anhydrides.
6. A polyester resin composition as claimed in claim 1, 2, 3, 4 or 5, wherein the one or more dihydric and/or polyhydric alcohol(s) employed in the formation of the polyester are glycols. 20
7. A process according to claim 6, wherein there is employed up to 110 mole percent of one or more glycols in the formation of said polyester.
8. A polyester resin composition as claimed in any one of claims 1 to 7, wherein the polyester has a molecular weight in the range from about 1500 to about 3500 and an acid number ranging from about 20 to about 35. 25
9. A polyester resin composition as claimed in any one of claims 1 to 8, wherein the polyester resin has a monomer compatibility of up to 25% and an alpha, beta-unsaturation (—C=C—) equivalent weight ranging from about 200 to about 275.
10. A polyester resin composition as claimed in any one of claims 1 to 9, wherein the monomer used in forming the polyester resin is styrene or vinyl toluene or a mixture thereof and constitutes from 40 to 60 weight percent of the total weight of the polyester resin. 30
11. A polyester resin composition as claimed in claim 10, wherein the monomer constitutes from 45 to 55 weight percent of the total weight of the polyester resin.
12. A polyester resin composition as claimed in any one of claims 1 to 11, wherein the cellulose ester resin is one which causes the mixture when cured to be opaque. 35
13. A polyester resin composition as claimed in any one of the preceding claims, wherein the cellulose ester resin is a cellulose acetate butyrate resin.
14. A polyester resin composition as claimed in claim 13, wherein said homogeneous mixture contains from 4 to 10 parts by weight of the cellulose acetate butyrate resin per 100 parts of the polyester resin. 40
15. A polyester resin composition as claimed in claim 14, wherein said homogeneous mixture contains from 5 to 8 parts by weight of the cellulose acetate butyrate resin per 100 parts of the polyester resin.
16. A polyester resin composition as claimed in claim 13, 14 or 15, wherein there is used a cellulose acetate butyrate resin having an average butyrate content of at least 44 percent by weight. 45
17. A polyester resin composition as claimed in claim 16, wherein there is used a cellulose acetate butyrate resin having an average butyrate content ranging from about 49 to about 55 percent by weight.
18. A polyester resin composition as claimed in claim 1, substantially as described in any one of the foregoing Examples. 50
19. A process for producing a reinforced polyester resin product which process comprises pultruding a polyester resin composition as claimed in any one of the preceding claims.
20. A reinforced polyester resin product whenever produced from the composition claimed in any one of claims 1 to 18 or by the process claimed in claim 19. 55