



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> PROCESS OF MAKING INJECTION MOLDED PARTS WITH HIGH TEMPERATURE DIMENSIONAL STABILITY		
<b>(57) Abstract</b>  The application discloses a process for making a precision engineered injection molded article. In one embodiment, the process comprises first molding a part from a polymer composite which contains polyethylene terephthalate and surface-treated glass fiber and mica. The article exhibits excellent dimensional stability even when subjected to temperatures between the glass transition temperature of the polyethylene terephthalate and 250 °C for about 30 minutes.		

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**PROCESS OF MAKING INJECTION MOLDED PARTS WITH HIGH  
TEMPERATURE DIMENSIONAL STABILITY**

**Field of the Invention**

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This invention relates to a novel process of making molded articles, with high temperature dimensional stability, from a suitable injection moldable thermoplastic resin. More specifically, it discloses a process of making parts from an injection moldable polyester which additionally  
10 contains sized glass fiber and mica. Such a process surprisingly yields parts with significantly reduced warpage.

**Background of the Invention**

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The art of making injection molded parts from thermoplastic resins is well known. Generally, parts molded from thermoplastic resins lack high temperature dimensional stability. Several attempts have been made to improve such stability by adding fillers to the resin. See, for example, D. Rosato, "Reinforced Plastics", *Encyclopedia of Polymer Science and  
20 Engineering*, Vol. 14, pages 327-391, John Wiley & Sons, New York (1988). Many such reinforced thermoplastics are commercially available. An example is the IMPET<sup>®</sup> brand reinforced moldable polyester resin available from Hoechst Celanese Corporation, Somerville, New Jersey. This resin comprises polyethylene terephthalate reinforced with about  
25 30% glass fiber. The IMPET<sup>®</sup> 830 resin comprises polyethylene terephthalate, glass and mica.

Several modifications have been attempted over the years in the composition of such resins. For example, U.S. Pat. No. 5,026,760 discloses thermoplastic polyester compositions glass fibers and/or mineral fillers. The latter may be mica which may be treated with a silane coupling agent. This treatment is often referred to in the industry as "sizing".

U.S. Pat. No. 4,861,515 discloses polyester compositions containing an inorganic filler such as, for example, mica, which has been surface-treated with an epoxysilane compound.

U.S. Pat. No. 4,386,027 discloses polyester compositions containing a flame retardant and finely divided mica or clay, and optionally glass fiber. The clay may be surface-treated with an aminosilane.

U.S. Pat. No. 5,147,920 discloses polyester compositions containing glass fibers, talcum and a brominated polystyrene.

U.S. Pat. No. 4,442,243 discloses thermoplastic composites reinforced with mica. The mica may be treated with  $\gamma$ -aminopropyltriethoxysilane. This patent emphasizes polypropylene compositions.

U.S. Pat. No. 4,560,715 discloses injection moldable thermoplastic resins, e.g. polyester resins, containing mica flakes, and optionally glass fibers. The mica may be surface-treated with  $\gamma$ -aminopropyltriethoxysilane.

U.S. Pat. No. 4,414,352 discloses thermoplastic molding compositions containing a polyester, a copolymer of ethylene and vinyl

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acetate in combination with an aromatic polycarbonate, polyethylene terephthalate, a flame retardant, and a mineral filler and optionally a reinforcing glass. The mineral filler may be mica which may be treated with a suitable aminosilane.

5           While such modifications in the resin compositions have yielded parts with somewhat improved performance over parts from nonreinforced injection moldable thermoplastics, there are still certain disadvantages with such materials, particularly in high temperature stability. There is still a great need for parts which possess dimensional stability at high  
10           temperatures. The need is particularly great for large parts which are dimensionally stable and undergo significantly reduced warpage under high temperature conditions.

          It is therefore, an object of this invention to provide a process to make injection molded polymeric parts with significantly reduced warpage  
15           at temperatures between the glass transition temperature ( $T_g$ ) of the polymer and 250° C.

          It is a further object of this invention to provide a process to make injection molded polymeric parts from thermoplastic resins with significantly reduced warpage at temperatures between the glass  
20           transition temperature ( $T_g$ ) of the polymer and 250° C.

          It is yet another object of this invention to provide a process to make injection molded from thermoplastic polyester resins, which parts

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possess significantly reduced warpage at temperatures between the glass transition temperature ( $T_g$ ) of the polymer and 250° C.

Other objects and advantages of the present invention will be apparent from the accompanying description and examples.

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**Summary of the Invention**

One or more of the foregoing objects are achieved by the provision of the present process of making a precision engineered injection molded article which process comprises: (a) providing an injection moldable  
10 polymer composite which consists essentially of 30 to 85 weight percent of a suitable polymer, 10 to 50 weight percent of a suitable reinforcing agent, which has been surface-treated with a suitable sizing agent, and 5 to 35 weight percent of a suitable filler material which has also been surface-treated with a suitable sizing agent which may or may not be the  
15 same as the sizing agent for the reinforcing agent; and (b) injection molding a part from said polymer composite. A part so processed surprisingly exhibits high temperature dimensional stability. High temperature dimensional stability is defined herein as nominal deformation of equal to, less than but not more than 1 millimeter when the  
20 part is subjected to temperatures between the glass transition temperature ( $T_g$ ) of the polymer and 250° C for about 30 minutes. The inventive process is suitable to prepare large parts which possess such stability.

## 5

Suitable polymers to prepare the composite include polyesters, polyphenylene sulfide, polyarylates, nylon, and the like. Suitable reinforcing agents include glass fiber, ceramic fiber, carbon fiber, and the like. Suitable filler materials include mica, talcum, clay, titanium dioxide, and the like, while suitable sizing agents include silanes such as, for example,  $\gamma$ -aminopropyltriethoxysilane, vinyltrimethoxysilane, vinyl triacetoxysilane, and the like.

The invention further discloses parts made by the above-described process.

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Description of the Invention

In one embodiment, the present invention teaches a process to make precision engineered molded parts which have high dimensional stability which, as defined above, is nominal deformation of not more than 1 millimeter when the part is subjected to temperatures between the glass transition temperature ( $T_g$ ) of the polymer and 250° C for about 30 minutes. The process comprises preparing a composite of a suitable polymer with a suitable reinforcing agent that has been sized and a suitable filler material that has also been sized and molding the composite under suitable conditions to yield the desired part.

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Suitable polymers are thermoplastics which are known to be amenable to molding to prepare parts. Such polymers should have the requisite stability to the molding conditions as is well known to those with

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skill in the art. Such polymers include, but are not limited to, polyesters, polyphenylene sulfide, nylon, polyarylate, polycarbonate, polyamide and the like, and mixtures thereof. The process is particularly suitable to polyesters. Suitable polyesters include, but are not limited to,

5 polyethylene terephthalate ("PET"), polybutylene terephthalate ("PBT"), poly(ethylene-2,6-naphthalate, "PEN"), polyethylene naphthalate bibenzoate (PENBB), poly(1,4-cyclohexanedimethanol terephthalate) ("PCT"), the THERMX<sup>®</sup> brand polyester (available from Eastman Chemicals, Kingsport, Tennessee), the VALOX<sup>®</sup> brand polyester

10 (available from General Electric Company, Pittsfield, Massachusetts), 1,4-cyclohexanedimethanol terephthalate, liquid crystal polymers ("LCPs") such as, for example, the VECTRA<sup>®</sup> brand LCP (available from Hoechst Celanese Corporation, Somerville, New Jersey), copolyesters such as, for example, poly(1,4-cyclohexylenedimethylene terephthalate-co-

15 isophthalate), poly (ethylene terephthalate-co-ethylene naphthalate, "PETN"), and the like. PET and PBT are the most preferred due to their large availability as well as the fact that molding of such resins are well known in the industry.

The amount of the polymer in the composite ranges generally from

20 30 to 85 weight percent. Preferred ranges are from 45 to 70 weight percent, while the typical ranges are from 45 to 60 weight percent.



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Suitable reinforcing agents include, for example, glass fiber, carbon fiber, ceramic fiber, and the like. Glass is the most preferred. While fiber is the most preferred form for the reinforcing agent, other suitable forms may also be employed in the practice of the invention. If the reinforcing agent is in the form of a fiber, the length of the fiber ranges generally from 1-10 mm, preferably from 2-6 mm and typically from 3-5 mm. The diameter of the fiber ranges generally from 6-30 $\mu$ m, preferably from 10-21  $\mu$ m, and typically from 11-16  $\mu$ m. The reinforcing agent is employed in the composite generally in the range 10-50 weight percent, preferably 15-40 weight percent, and typically 25-35 weight percent.

Suitable fillers include, but are not limited to, mica, talcum, clay, titanium dioxide and the like. There may be variants within the same filler type such as, for example, the muscovite type mica (supplied by KMG Minerals, Inc., Kings Mountain, North Carolina), the phlogopite type mica (from Suzorite, Inc., Boucherville, Quebec, Canada) and the like. The size of the filler particles is in the general range of 20-500  $\mu$ m, preferably in the range 30-100  $\mu$ m and typically 40-60  $\mu$ m. The filler is employed in the composite generally in the range 5-35 weight percent, preferably 7-25 weight percent, and typically 10-20 weight percent.

As stated above, both the reinforcing agent and the filler are sized prior to preparing the polymer composite. Sizing is well known in the industry. In the inventive process, sizing of the reinforcing agent and filler

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are performed with a suitable sizing agent. Preferred sizing agents are silanes such as, for example,  $\gamma$ -aminopropyltriethoxysilane, vinyl-tris(b-methoxyethoxy) silane, octadecyl vinyl silane, g-methacryloxypropyltrimethoxysilane, vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriacetoxysilane, g-chloropropyltrimethoxysilane, b-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and the like, as well as mixtures thereof.

The composite may contain additional materials as will be obvious to those skilled in the art. Some of them include, for example, antioxidants, stabilizers, lubricants, nucleating agents, impact modifiers and the like. Examples of suitable antioxidants include phosphites. Examples of suitable stabilizers include bis-phenol A based epoxy compounds. Examples of suitable lubricants include olefinic waxes. Examples of suitable nucleating agents include sodium salts of suitable acids. Examples of suitable impact modifiers include low melting elastomers.

The invention is described below with reference to a composition prepared from a polyester, for example, PET. The reinforcing agent used is glass fiber and the filler is mica. Both the glass fiber and mica are sized with  $\gamma$ -aminopropyltriethoxysilane. The composition may be prepared by first dry mixing the above three components. As stated before, other

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ingredients may also be added into this composition. While glass fiber may be mixed in at this stage, preferably it is fed downstream during the extrusion process, while all others are mixed prior to feeding into the main feeder.

5           The extrusion may be carried out in a suitable extruder such as for example a twin screw extruder with down-stream feeding capability. Many such extruders are commercially available such as, for example, the 40 mm screw size (as well as the 30 mm screw size) Werner Pfleidererr twin screw extruder (Model ZSK from Werner Pfleidererr Corporation, Ramsey,  
10   New Jersey). The extruder may be fed with the resin and additives stated above at the main feeder while the glass is fed downstream. The machine temperature is kept at a suitable level. For PET, for example, the temperature may range 250 - 300°C. The material is compounded and then extruded into a suitable shape such as, for example, pellets. The  
15   pellets may then be injection molded into suitable parts.

          Dimensional stability at a desired temperature, for example, 200°C, may be determined by methods known to those skilled in the art, or preferably by subjecting a molded test piece to a specified force while being held isothermally at 200°C in a three point bending fixture. An  
20   instrument such as, for example, the Perkin Elmer Model Number DMA7E (from Perkin-Elmer Corporation, Norwalk, Connecticut) may be used for this measurement. The flexural deflection may be measured at, for

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example, 15 and 30 thirty minutes. This is referred to as the flexural strain. The test specimen is placed on knife edge supports at the two ends producing a supported span of about 20 mm. A knife edged probe across the width of the specimen is lowered onto the topside of the piece  
5 producing the three point bending configuration. A force of about 7000 millinewtons is applied to the to the specimen by the top probe and the temperature is rapidly raised to 200°C. The deformation of the test piece is monitored by recording the probe position continuously during the 30 minute isothermal program. The probe position at 15 and 30 minutes is  
10 used to calculate strain and to rank the performance of materials. A lower absolute strain indicates a material with higher dimensional stability at 200°C.

For comparison, a composite is prepared with the same polyester resin, glass fiber but with unsized mica, and then extruded and molded  
15 into a part and its strain is evaluated similar to above. In a typical actual experiment, a part from a comparative resin exhibited higher strain and/or unacceptable warpage at 200°C, while a similar part from an inventive resin (with sized mica) exhibited much lower strain and substantially reduced warpage at 200°C. In the laboratory comparative experiment, the  
20 three point bending test, the inventive test piece maintained an absolute flexural strain of less than 2.0% than the comparative piece under the

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same conditions (temperatures of 200° C for at least 30 minutes). More details are described in the EXAMPLES section below.

The invention is further illustrated with EXAMPLES below. The Examples are for illustrative purposes only and not to be construed as  
5 limiting the invention in any way.

EXAMPLES

In the following Examples, PETN8 refers poly(ethylene  
10 terephthalate-co-ethylene naphthalate) containing 8 mole percent of the naphthalate. The terms "kpsi" refers to kilopounds per square inch, HDT to heat deflection temperature and "psi" to pounds per square inch. Impact resistance is expressed as Notched Izod. Sizing of the glass and mica were performed with  $\gamma$ -aminopropyltriethoxysilane by methods known in  
15 the literature. A Werner Pfeidererr twin screw extruder (Model Number ZSK) was used for compounding. All crystallinity evaluations were performed with a Perkin-Elmer DSC 7 instrument (available from Perkin-Elmer Corporation, Norwalk, CT).

20 Examples 1-3. Comparative Examples using unsized mica: A dry mixture of the polyester, lubricants, stabilizers, antioxidants and nucleating agents as shown in Table 1 was fed into the main feeder of the extruder while glass was added downstream. The compounding was performed in the twin screw extruder at 270 °C. The extrudate was pelletized and dried.

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The dried pellets were then injection molded at 280 °C for testing. The formulations and properties of the molded parts are shown in TABLE 1.

TABLE 1

Compositions comprising polyester, glass, lubricants, stabilizers, antioxidants, nucleating agents.			
	Example Number		
	1	2	3
<u>Composition (weight percentage)</u>			
PET	67		
PEN		67	
PETN8			67
Glass (14 mm in diameter, 1/8" long), sized	30	30	30
Antioxidant	0.2	0.2	0.2
Stabilizer	0.4	0.4	0.4
Lubricant	2	2	2
Nucleating Agent	0.4	0.4	0.4
<u>Properties of molded part</u>			
Tensile strength (kpsi)	23.81	23.30	23.20
Break Elongation (%)	2.15	2.27	2.15
Flexural Strength (kpsi)	36.69	34.23	31.70
Flexural modulus (kpsi)	156.0	134.0	148
Notched Izod Impact (ft-lb/in)	1.38	1.76	1.68
Unnotched Izod Impact (ft-lb/in)	12.79	10.87	13.03
HDT at 264 psi (°C)	221	113	165
Crystallinity (wt %)	-	-	-
Strain at 15 min (absolute %)	4.78	147.6	4.30
Strain at 30 min (absolute %)	4.94	147.8	7.12

Although Example 1 which contains PET as the polymer matrix has low strain at both 15 and 30 minutes and high HDT, the part from Example 1 warps at 200°C. The parts from Examples 2 and 3 have poor dimensional stability at 200°C.

## 13

Examples 4-8. Inventive compositions containing sized filler and parts  
therefrom: Compositions similar to above Examples were prepared but  
with added filler (mica) which had been sized with  $\gamma$ -  
aminopropyltriethoxysilane. The extrusion and injection molding to parts  
5 were performed similar to the prior Examples. The formulations and  
properties of the molded parts are shown in **TABLE 2**.

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TABLE 2

Compositions comprising polyester,  
glass, lubricants, stabilizers,  
antioxidants, nucleating agents.

	Example Number				
	4	5	6	7	8
<b>Composition (weight percentage)</b>					
PET	56.5		56.5	56.5	56.5
PETN8		56.5			
Glass (14 mm in diameter, 1/8" long)	22.25	22.25	22.25	22.25	22.25
Muscovite mica (135 mesh, no sizing)	13.25	13.25			
Sized Muscovite mica (135 mesh)			13.25		
Phologopite mica (135 mesh, unsized)				13.25	
Sized Phologopite mica (135 mesh)					13.25
Impact Modifier	5	5	5	5	5
Antioxidant	0.2	0.2	0.2	0.2	0.2
Stabilizer	0.4	0.4	0.4	0.4	0.4
Lubricant	2	2	2	2	2
Nucleating Agent	0.4	0.4	0.4	0.4	0.4
<b>Properties</b>					
Tensile strength (kpsi)	16.84	14.79	17.12	17.16	17.49
Break Elongation (%)	1.9	1.70	2.1	1.97	1.96
Flexural strength (kpsi)	26.23	22.22	26.53	25.78	26.15
Flexural modulus (kpsi)	148	128	141	139	140
Notched Izod Impact (ft-lb/in)	1.26	1.25	1.34	1.12	1.18
Unnotched Izod Impact (ft-lb/in)	11.20	10.10	12.06	9.53	10.00
HDT at 264 psi (°C)	198	84	201	207	216
Crystallinity (wt %) <sup>1</sup>				32.9	31.2
Strain at 15 min (absolute %)	1.72	6.55	0.84	3.38	4.65
Strain at 30 min (absolute %)	1.97	6.74	0.99	3.50	4.81

The results in TABLE 2 demonstrate that using sized mica leads to higher HDT and lower strains at 15 and 30 minutes, showing better dimensional stability.

<sup>1</sup> All the crystallinity studies were carried out on a Perkin-Elmer DSC 7. The bar samples were heated at 10°C/me to 290°C to measure the crystallinity of the polymer matrix. Crystallinity was then calculated based on the amount of polymer in the composition.



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Examples 9-13. Effect of increasing the amounts of sized glass and sized mica: In Examples 9-13, the levels of the sized glass and sized mica were increased to more than in Examples 4-8. TABLE 3 summarizes the formulations and the properties of molded parts.

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TABLE 3

Compositions comprising polyester,  
glass, lubricants, stabilizers,  
antioxidants, nucleating agents.

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	Example Number				
	9	10	11	12	13
<u>Composition (weight percentage)</u>					
PET	47	47	47	47	52
Glass (14 mm in diameter, 1/8" long)	30	30	30	30	30
Muscovite mica (135 mesh, no sizing)	15				
Sized Muscovite mica (135 mesh)		15			15
Phologopite mica (135 mesh, unsized)			15		
Sized Phologopite mica (135 mesh)				15	
Antioxidant	0.2	0.2	0.2	0.2	0.2
Stabilizer	0.4	0.4	0.4	0.4	0.4
Lubricant	2	2	2	2	2
Nucleating Agent	0.4	0.4	0.4	0.4	0.4
<u>Properties</u>					
Tensile strength (kpsi)	17.83	17.65	18.85	18.61	19.79
Break Elongation (%)	1.59	1.78	1.90	2.39	2.36
Flexural strength (kpsi)	25.85	25.83	27.90	26.67	28.59
Flexural modulus (kpsi)	188	182	179	183	209
Notched Izod Impact (ft-lb/in)	1.10	1.18	1.21	1.21	1.17
Unnotched Izod Impact (ft-lb/in)	6.72	6.91	9.26	9.07	7.05
HDT at 264 psi (°C)	220	217	221	214	220
Crystallinity (wt %)*	32.1	31.3	33.6	29.8	
Strain at 15 min (absolute %)	2.62	2.00	2.37	1.70	0.25
Strain at 30 min (absolute %)	2.75	2.12	2.50	1.80	0.37

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The results demonstrate that higher levels of the glass and filler improve the dimensional stability further.

CLAIMS

What is claimed is:

- 5 1. A process of making a large precision engineered injection molded article, said process comprising: (a) providing a polymer composite which consists essentially of 30 to 85 weight percent of a polymer resin, 10 to 50 weight percent of a reinforcing agent, and 5 to 35 weight percent of a filler material, wherein said reinforcing agent and said filler material have been
- 10 surface-treated with a suitable silane reagent; and (b) injection molding said article from said polymer composite, wherein said precision engineered injection molded article maintains a nominal deformation of not more than 1 mm when subjected to temperatures between the glass transition temperature of said polymer resin and 250° C for at least 30
- 15 minutes.
2. The process as described in claim 1, wherein said polymer resin is selected from the group consisting of polyester, polyphenylene sulfide, nylon, polyarylate, polycarbonate, polyamide, and mixtures thereof.
- 20
3. The process as described in claim 2, wherein said polymer resin is a polyester.

4. The process as described in claim 3, wherein said polyester is selected from the group consisting of polyethylene terephthalate, polybutylene terephthalate, poly(ethylene-2,6-naphthalate, polyethylene naphthalate bibenzoate, 1,4-cyclohexanedimethanol terephthalate, liquid  
5 crystal polyester, poly(1,4-cyclohexylenedimethylene terephthalate-co-isophthalate), poly (ethylene terephthalate-co-ethylene naphthalate) and mixtures thereof.
5. The process as described in claim 4, wherein said polyester is  
10 polyethylene terephthalate.
6. The process as described in claim 4, wherein said polyester is polybutylene terephthalate.
- 15 7. The process as described in claim 1, wherein said reinforcing agent is selected from the group consisting of glass fiber, carbon fiber, ceramic fiber, and combinations thereof.
8. The process as described in claim 7, wherein said reinforcing agent  
20 is glass fiber.

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9. The process as described in claim 1, wherein said reinforcing agent has a length in the range 1-10 mm and diameter in the range 6-30  $\mu\text{m}$ .
10. The process as described in claim 1, wherein said filler material is  
5 selected from the group consisting of mica, talcum, clay, and combinations thereof.
11. The process as described in claim 10, wherein said filler material is mica.  
10
12. The process as described in claim 1, wherein said filler has a size in the range 20-500  $\mu\text{m}$ .
13. The process as described in claim 1, wherein said silane reagent is  
15 selected from the group consisting of  $\gamma$ -aminopropyltriethoxysilane, vinyltris(b-methoxyethoxy) silane, octadecyl vinyl silane, g-methacryloxypropyltrimethoxysilane, vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriacetoxysilane, g-chloropropyltrimethoxysilane, b-(3,4-epoxycyclohexyl)  
20 ethyltrimethoxysilane and mixtures thereof.

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14. The process as described in claim 13, wherein said silane reagent is  $\gamma$ -aminopropyltriethoxysilane.

15. The process as described in claim 1, wherein said polymer  
5 composite further contains antioxidants, stabilizers, lubricants, nucleating agents, impact modifiers and combinations thereof.

16. The process as described in claim 1, wherein said polymer resin is present in amounts of 45-70 weight percent in said composite.

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17. The process as described in claim 1, wherein said polymer resin is present in amounts of 45-60 weight percent in said composite.

18. The process as described in claim 1, wherein said reinforcing agent  
15 is present in amounts of 15-40 weight percent in said composite.

19. The process as described in claim 1, wherein said reinforcing agent is present in amounts of 25-35 weight percent in said composite.

20 20. The process as described in claim 1, wherein said filler material is present in amounts of 7-25 weight percent in said composite.

**20**

21. The process as described in claim 1, wherein said filler material is present in amounts of 10-20 weight percent in said composite.

22. A precision engineered article prepared by the process of claim 1.

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23. A process of making a precision engineered injection molded article, said process comprising: (a) providing a polymer composite which consists essentially of 30 to 85 weight percent of polyethylene terephthalate, 10 to 50 weight percent of glass fiber, and 5 to 35 weight percent of mica, wherein said glass fiber and said mica have been surface-treated with a suitable silane reagent; and (b) injection molding said article from said polymer composite, wherein said precision engineered injection molded article maintains a nominal deformation of not more than 1 mm when subjected to temperatures between the glass transition temperature of said polyethylene terephthalate and 250° C for at least 30 minutes.

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24. A process of making a precision engineered injection molded article, said process comprising: (a) providing a polymer composite which consists essentially of 30 to 85 weight percent of polybutylene terephthalate, 10 to 50 weight percent of glass fiber, and 5 to 35 weight percent of mica, wherein said glass fiber and said mica have been

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surface-treated with a suitable silane reagent; and (b) injection molding said article from said polymer composite, wherein said precision engineered injection molded article maintains a nominal deformation of not more than 1 mm when subjected to temperatures between the glass transition temperature of said polyethylene terephthalate and 250° C for at least 30 minutes.

25. A precision engineered article prepared by the process of claim 23.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/05605

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08K9/06

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K C08L

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 188 (C-295), 3 August 1985 & JP 60 058465 A (KARUPU KOGYO KK), 4 April 1985, see abstract	1,7,8, 15-17,22
Y	---	
Y	PATENT ABSTRACTS OF JAPAN vol. 012, no. 450 (C-547), 25 November 1988 & JP 63 175059 A (MITSUBISHI RAYON CO LTD), 19 July 1988, see abstract	1-8,10, 11,15-25
Y	---	
Y	KATZ, H.S. ET AL.: "Handbook of fillers for plastics" 1987 XP002034863 see page 65 - page 76 see page 65, left-hand column, paragraph 1 ---	1-8,10, 11,15-25
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

9 July 1997

Date of mailing of the international search report

29.07.97

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/05605

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 013, no. 105 (C-575), 13 March 1989 & JP 63 280762 A (MITSUBISHI RAYON CO LTD), 17 November 1988, see abstract ---	1-8,10, 11,15-25
Y	US 4 386 027 A (COHEN STUART C) 31 May 1983 cited in the application see column 5, paragraph 1; example 1 ---	1-8,10, 11,15-25
Y	US 5 147 920 A (DEKKERS THEODORUS A M ET AL) 15 September 1992 cited in the application see claim 2; examples C,D ---	1-8,10, 11,15-25
A	US 4 414 352 A (COHEN STUART C ET AL) 8 November 1983 cited in the application see table 2 -----	1

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Information on patent family members

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