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(54) Title: **Use of Phase Change Materials in Thermoplastic Polymers**

(57) Summary:

Use of phase change materials in thermoplastic polymers.

The present invention relates to parts consisting of a thermoplastic resin characterized by the fact that its matrix and/or surface comprises at least one phase-change inorganic material and because the glass transition temperature of the thermoplastic resin (calculated by DSC) is 2 to 20ºC higher than the melting temperature of the phase-change inorganic material.

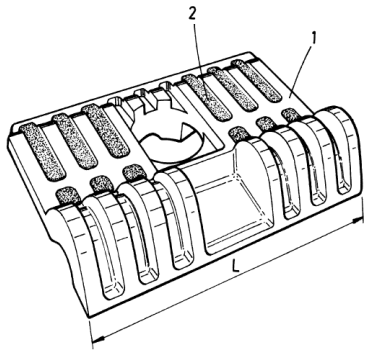

FIG.1

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DESCRIPTION

USE OF PHASE CHANGE MATERIALS IN THERMOPLASTIC POLYMERS

The present invention relates to the use of phase-change materials in thermoplastic polymers. Therefore, the invention could be framed in the field of materials science and technology, more specifically in the field of thermoplastic polymeric materials.

STATE OF THE ART

Thermoplastic polymers subjected to cyclic mechanical stresses may have their fatigue resistance reduced by the appearance of cracks. The cyclic mechanical stress produces an increase in temperature that modifies the flexibility and mechanical behavior of these materials.

The use of thermoplastic polymers in engineering parts is restricted when temperature values that exceed the transition value Tg, characteristic of each material, are reached. For example, in the case of dry polyamide 6.6 (PA 6.6), the Tg (calculated by DSC, from the English *Differential Scanning Temperature,* with a heating ramp of 10°C/min in a nitrogen atmosphere) is set at 53 °C, which means that when the part reaches higher temperatures, defects may appear that worsen its mechanical properties.

In general, when polymeric parts are used, it is common to increase the temperature of use by increasing the percentage of their fibre reinforcement, for example with glass fibres, although this circumstance penalises the toughness of the composite material.

Therefore, it is necessary to increase the operating temperature range of engineering polymeric parts in a way that does not imply an increase in its fragility.

Phase Change Materials *(PCMs)* are materials with high latent heat that store or release large amounts of energy at the phase change temperature (s6lido - Humidity).

During the phase change, the temperature remains constant while the material absorbs or releases energy. The main application of these PCMs is their use in construction for thermal energy storage (Sharmaet *al., Renewable and Sustainable Energy Reviews* 13, (2009), 318-345).

DESCRIPTION OF THE INVENTION

The present invention relates to the use of phase change materials in thermoplastic polymers.

The parts of the invention have the following advantages:

- they have greater fatigue resistance than parts of the same thermoplastic queen without inorganic materials with phase change;
- the phase-change materials that can be used in the invention are abundant;
- The procedure for obtaining the parts of the invention is simple and not it requires great adaptations in the production of these pieces;
- the small amount of the phase-change material to be incorporated, will not influence significantly in the final cassette of the pieces.

Therefore, a first aspect of the present invention refers to a part made up of a thermoplastic resin characterized by the fact that its matrix and/or surface includes at least one inorganic material with a change phase; y

the transition temperature of the thermoplastic resin, calculated by DSC with a heating ramp of 10°C/min in the nitrogen atmosphere,

is 2 to 20°C higher than the melting temperature of inorganic material with phase change.

Inorganic material with phase change is defined as inorganic materials with high latent heat that at the phase change temperature store or release large amounts of energy. They are classified between hydrates and metals.

In a realization of the first aspect of the present invention, the glass transition temperature of the thermoplastic resin, calculated by DSC with a heating ramp of 10°C/min in nitrogen atmosphere, is 5°C to 10°C higher than the melting temperature of inorganic material with phase change.

In a realization of the first aspect of the present invention, the resin thermoplastic is selected from polyamide, polyoxymethylene, polyethylene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene, polyacrylonitrile-styrene-acrylate, polyvinyl chloride, polyphenylene sulphide, polymethylmethacrylate, polycarbonates, polyethylene terephthalate, polybutylene terephthalate, thermoplastic elastomers and any of their mixtures,
preferably thermoplastic resin is selected from acrylonitrile-butadiene-styrene, polyacrylonitrile, polystyrene, polyvinyl chloride, polyphenylene sulfide, polyethylene terephthalate, polymethylmethacrylate, and polyamide, but preferably thermoplastic resin is polyamide, and more preferably thermoplastic resin is selected from polyamide 6.6,
polyamide 11 and polyamide 6.10.

In a realization of the first aspect of the present invention, the thermoplastic resin is glass fibre reinforced polyamide, as it is an engineering polymer commonly used in high-quality technical applications.
responsibility.

In a realization of the first aspect of the present invention, the phase-change inorganic material is a hydrate. Preferably the inorganic material with phase change is selected from the hydrates in the following list, and any of their combinations:

5

PCM inor anico hydrate	Tt" °C
MgCl2.6H2O	117,0
KAl(SQ4)2.12H2O	91,0
Mg(NQ3)2.6H2O	89,9
Ba(OH)2.8H2O	78,0
Al(NQ3)2.9H2O	72,0
LiCH3CQO.2H2O	70,0
Na3PQ4.12H2O	65,0
NaOH.H2O	64,3
NaAl(SO4)2.1 0H2O	61,0
Fe(NQ3)2.2H2O	60,5
CH3CQONa.3H2O	58,0
MgCl2.4H2O	58,0
MnCl2.4H2O	58,0
Ni(NQ3)2.6H2O	57,0
FeCb.2H2O	56,0
Zn(NQ3)2·2H2O	55,0
Ca(NQ3)2.3H2O	51,0
Na2S2O3.5H2O	48,5
MgSO4.7H2O	48,5
K2HPO4.3H2O	48,0
Na2SiQ3.5H2O	48,0
Fe(NQ3)3.9H2O	47,0
Ca(NQ3).4H2O	47,0
Mg(NO3)2.4H2O	47,0
Zn(NQ3)2.4H2O	45,0
K2HPQ4.7H2O	45,0
Cal2.6H2O	42,0

Mgl2.8H2O	42,0
KF.2H2O	42,0
CoSO4.7H2O	40,7
Na2HPQ4.12H2O	40,0
Mn(NQ3)2.4H2O	37,1
FeCb.6H2O	37,0
Zn(NQ3)2.6H2O	36,1
LiBr2.2H2O	34,0
CaBr2.6H2O	34,0
KFe(SQ4)2·12H2O	33,0
Na2SQ4.10H2O	32,4
Na2CO3.10H2O	32,0
LiNO3.3H2O	30,0
LiNQ3.2H2O	30,0
CaCl2.12H2O	29,8
Fe8r3.6H2O	27,0
Mn(NQ3)2.6H2O	25,5
K2HPQ4.6H2O	14,0

*Tt: Melting Temperature

Table 1 shows combinations of thermoplastic resins and phase-change inorganic materials that can be used with each thermoplastic resin to improve the mechanical properties of the resin:

Thermoplastic	**Tg(°C)***	**Inorganic PCM**	**TfPcM(°C)**	**Tg-Tf**
Acrylonitrile-Butadiene-Styrene	110	KAl(SQ4)2.12H2O	91,0	19,0
Polyacrylonitrile	104	Mg(NQ3)2.6H2O	89,9	14,1
Polystyrene	100	Mg(NQ3)2.6H2O	89,9	10,1
Polyvinyl chloride	87	Ba(OH)2.8H2O	78,0	9,0
		Al(NQ3)2.9H2O	72,0	15,0
		LiCH3CQO.2H2O	70,0	17,0

Polyphenylene sulfide	85	Ba(OH)2.8H2O	78,0	7,0
		Al(NQ3)2.9H2O	72,0	13,0
		LiCH3CQO.2H2O	70,0	15,0
		Na3PQ4.12H2O	65,0	20,0
Polyethylene Terephthalate	69	Na3PQ4.12H2O	65,0	4,0
		NaOH.H2O	64,3	4,7
		NaAl(SQ4)2.10H2O	61,0	8,0
		Fe(NQ3)2.2H2O	60,5	8,5
		CH3CQONa.3H2O	58,0	11,0
		MgCl2.4H2O	58,0	11,0
		MnCl2.4H2O	58,0	11,0
		Ni(NQ3)2.6H2O	57,0	12,0
		FeCb.2H2O	56,0	13,0
		Zn(NQ3)2·2H2O	55,0	14,0
		Ca(NQ3)2.3H2O	51,0	18,0
Polymethylmethacrylate	60	CH3CQONa.3H2O	58,0	2,0
		MgCl2.4H2O	58,0	2,0
		MnCl2.4H2O	58,0	2,0
		Ni(NQ3)2.6H2O	57,0	3,0
		FeCl3.2H2O	56,0	4,0
		Zn(NQ3)2.2H2O	55,0	5,0
		Ca(NQ3)2.3H2O	51,0	9,0
		Na2S2O3.5H2O	48,5	11,5
		MgSO4.7H2O	48,5	11,5
		K2HPO4.3H2O	48,0	12,0
		Na2SiQ3.5H2O	48,0	12,0
		Fe(NQ3)3.9H2O	47,0	13,0
		Ca(NQ3).4H2O	47,0	13,0
		Mg(NQ3)2.4H2O	47,0	13,0
		Zn(NQ3)2.4H2O	45,0	15,0
		K2HPO4.7H2O	45,0	15,0
		Cal2.6H2O	42,0	18,0
		Mgl2.8H2O	42,0	18,0
		KF.2H2O	42,0	18,0
		CoSO4.7H2O	40,7	19,3
		Na2HPO4.12H2O	40,0	20,0
Polyamide 6.6	53	Ca(NQ3)2.3H2O	51,0	2,0
		MgSO4.7H2O	48,5	4,5

		Na2S2Q3.5H2O	48,5	4,5
		K2HPO4.3H2O	48,0	5,0
		Na2SiO3.5H2O	48,0	5,0
		Fe(NQ3)3.9H2O	47,0	6,0
		Ca(NQ3).4H2O	47,0	6,0
		Mg(NQ3)2.4H2O	47,0	13,0
		Zn(NQ3)2.4H2O	45,0	8,0
		K2HPQ4.7H2O	45,0	8,0
		Cal2.6H2O	42,0	11,0
		Mgl2.8H2O	42,0	11,0
		KF.2H2O	42	11,0
		CoSO4.7H2O	40,7	12,3
		Na2HPQ4.12H2O	40,0	13,0
		Mn(NO3)2.4H2O	37,1	15,9
		FeC'3.6H2O	37,0	16,0
		Zn(NQ3)2.6H2O	36,1	16,9
		LiBr2.2H2O	34,0	19,0
		CaBr2.6H2O	34,0	19,0
		KFe(SO4)2· 12H2O	33,0	20,0
Polyamide 11	45	Cal2.6H2O	42,0	3,0
		Mgl2.8H2O	42,0	3,0
		KF.2H2O	42,0	3,0
		CoSO4.7H2O	40,7	4,3
		Na2HPQ4.12H2O	40,0	5,0
		Mn(NQ3)2.4H2O	37,1	7,9
		FeCl3.6H2O	37,0	8,0
		Zn(NO3)2.6H2O	36,1	8,9
		LiBr2.2H2O	34,0	11,0
		CaBr2.6H2O	34,0	11,0
		Na2SO4.10H2O	32,4	12,6
		Na2CQ3.10H2O	32,0	13,0
		KFe(SQ4)2.12H2O	33,0	12,0
		LiNO3.3H2O	30,0	15,0
		LiNO3.2H2O	30,0	15,0
		CaC'2.12H2O	29,8	15,2
		Fe8r3.6H2O	27,0	18,0
		Mn(NQ3)2.6H2O	25,5	19,5
Polyamide 6.10	40	Mn(NQ3)2.4H2O	37,1	2,9
		FeC'3.6H2O	37,0	3,0

		Zn(NQ3)2.6H2O	36,1	3,9
		LiBr2.2H2O	34,0	6,0
		CaBr2.6H2O	34,0	6,0
		KFe(SQ4)2.12H2O	33,0	7,0
		Na2SO4.10H2O	32,4	7,6
		Na2CO3.10H2O	32,0	8,0
		LiNQ3.3H2O	30,0	10,0
		LiNQ3.2H2O	30,0	10,0
		CaCl2.12H2O	29,8	10,2
		Fe8r3.6H2O	27,0	13,0
		Mn(NQ3)2.6H2O	25,5	14,5

*Value determined through the DSC technique, with a heating ramp of 10°C/min in the nitrogen atmosphere.

In a realization of the first aspect of the present invention, the thermoplastic resin is acrylonitrile-butadiene-styro, and the phase-change inorganic material is KAl(SQ4)2· 12H2O.

In another embodiment of the first aspect of the present invention, the resin thermoplastic is polyacrylonitrile and the inorganic material with phase change is Mg(NQ3)2·6H2O.

In another embodiment of the first aspect of the present invention, the thermoplastic resin is polystyrene and the phase-change inorganic material is polystyrene.

Mg(NQ3)2·6H2O.

In another realization of the first aspect of the present invention, the thermoplastic resin is polyvinyl chloride and the phase-change inorganic material is selected from Ba(OH)2.8H2O, Al(NO3)2.9H2O, LiCH3CQO.2H2O, and

Any of its mixtures, preferably the thermoplastic resin is polyvinyl chloride and the inorganic material with phase change is Ba(OH)2.8H2O.

In another realization of the first aspect of the present invention, the thermoplastic resin is polyphenylene sulfide and the phase-change inorganic material is selected from Ba(OH)2.8H2O, Al(NQ3)2.9H2O, LiCH3COO.2H2ONa3PQ4.12H2O and any of their mixtures, preferably The thermoplastic resin is polyvinyl chloride and the inorganic material with phase change is Ba(OH)2.8H2O.

In another realization of the first aspect of the present invention, the thermoplastic resin is polyethylene terephthalate and the inorganic material with change of phase is selected from Na3PQ4.12H2O, NaOH.H2O,NaAl(SO4)2,10H2O, Fe(NQ3)2.2H2O, CH3CQONa.3H2O, MgCl2.4H2O, MnCl2.4H2O, Ni(NQ3)2.6H2O, FeCb.2H2O, Zn(NQ3)2.2H2O, Ca(NQ3)2.3H2O, and any of their mixtures, preferably the thermoplastic resin is polyethylene terephthalate and the inorganic material with phase change is selected from NaAl(SO4)2,10H2O, Fe(NQ3)2.2H2O and any of their mixtures.

In another realization of the first aspect of the present invention, the thermoplastic resin is polymethylmethacrylate and the phase-change inorganic material is selected from CH3CQONa.3H2O, MgCl2.4H2O, MnCl2.4H2O, Ni(NQ3)2.6H2O, FeCb.2H2O, Zn(NQ3)2.2H2O, Ca(NQ3)2.3H2O, Na2S2O3•5H2O, MgSO4.7H2O, K2HPO4.3H2O, Na2SiQ3.5H2O, Fe(NQ3)3.9H2O, Ca(NQ3).4H2O, Mg(NQ3)2.4H2O, Zn(NQ3)2.4H2O, K2HPQ4.? H2O, Cal2.6H2O, Mgl2.8H2O, KF.2H2O, CoSQ4.? H2O, Na2HPO4.12H2O and any of their mixtures, preferably the thermoplastic resin is polymethylmethacrylate and the material phase-change inorganic is selected from Zn(NQ3)2.2H2O, Ca(NQ3)2.3H2O and any of their mixtures.

In another realization of the first aspect of the present invention, the thermoplastic resin is polyamide 6.6 and the phase-change inorganic material is selects from Ca(NQ3)2.3H2O, MgSO4.7H2O, Na2S2Q3_5H2O, K2HPQ4.3H2O, Na2SiO3.5H2O, Fe(NQ3)3.9H2O, Ca(NQ3).4H2O,

Mg(NQ3)2.4H2O,Zn(NQ3)2.4H2O, K2HPO4.7H2O, Cal2.6H2O, Mgl2.8H2O,

KF.2H2O, CoSQ4.? H2O,Na2HPQ4_12H2O, Mn(NQ3)2.4H2O, FeC'3.6H2O, Zn(NQ3)2.6H2O, Li8r2.2H2O, Ca8r2.6H2O, KFe(SQ4)2.12H2O and any of its mixtures, preferably the thermoplastic resin is polyamide 6.6 and the inorganic material with phase change is selected from KzHPO4.3H2O, Na2SiQ3.5H2O, Fe(NO3)3.9H2O, Ca(NQ3).4H2O, Zn(NQ3)2.4H2O, KzHPO4.7H2O and any of its mixtures, but preferably the phase-change inorganic material is Na2SiQ3.5H2O.

In another embodiment of the first aspect of the present invention, the resin thermoplastic is 11 polyamide and the inorganic material with phase change is selected from Cal2.6H2O, Mgl2.8H2O, KF.2H2O, CoSQ4.? H2O, Na2HPQ4.12H2O, Mn(NQ3)2.4H2O, FeC'3.6H2O, Zn(NQ3)2.6H2O, Li8r2.2H2O, Ca8r2.6H2O, Na2SQ4.10H2O, Na2CQ3.10H2O, KFe(SQ4)2.12H2O, LiNQ3.3H2O, LiNO3.2H2O, CaCl2.12H2O, Fe8r3.6H2O, Mn(NQ3)2.6H2O and Any of its mixtures, preferably the phase-change inorganic material is selected from Na2HPQ4.12H2O, Mn(NQ3)2.4H2O, FeCb.6H2O, Zn(NQ3)2.6H2O and any of their mixtures.

In another embodiment of the first aspect of the present invention, the resin thermoplastic is polyamide 6.10 and the inorganic material with phase change is selected from Mn(NQ3)2.4H2O, FeC'3.6H2O, Zn(NQ3)2.6H2O, LiBr2.2H2O, Ca8r2.6H2O, KFe(SQ4)2.12H2O, Na2SO4.10H2O, Na2CO3.1 0H2O, LiNQ3.3H2O, LiNO3.2H2O, CaCl2.12H2O, Fe8r3.6H2O, Mn(NQ3)2.6H2O and

any of its mixtures, preferably the inorganic material with change phase is selected from Li8r2.2H2O, Ca8r2.6H2O, KFe(SQ4)2.12H2O, Na2SO4.10H2O, Na2CQ3.1 0H2O, LiNQ3.3H2O, LiNO3.2H2O y any of their mixtures.

In a realization of the first aspect of the present invention, the piece is selects stop, hinge, gear, screw, fixing clip, connector and clamp, preferably the part is a stop in a rail-cross fastening system.

In a realization of the first aspect of the present invention, the part selected is a stop in a rail-sleeper fastening system and the thermoplastic resin is polyamide 6, polyamide 6.6 and any of their mixtures,

preferably glass fibre reinforced polyamide 6, glass fibre reinforced polyamide 6.6, plus preferably glass fibre reinforced in percentages of 30-35% by weight, which are the resins approved by the Spanish railway administrations.

In a realization of the first aspect of the present invention, the part as defined above is characterized by the fact that its matrix includes the inorganic phase-change material. In other words, the inorganic material with a phase change has been included in the thermoplastic resin matrix itself before the part is formed.

In another realization of the first aspect of the present invention, the part as defined above is characterized by the fact that its surface comprises the inorganic phase-change material. Surprisingly, as illustrated in the examples of the invention, it has been seen that by putting the

Inorganic phase change material in surface contact with the thermoplastic resin part improves the fatigue resistance properties of the thermoplastic resin part. The fact that these mechanical improvements are achieved with a surface contact makes the use of these materials in combination with thermoplastic resins very attractive since the manufacturing method is simple and does not require

major modifications. A surface contact is thought to improve the mechanical properties of the thermoplastic resin part because heat exchange occurs on the contact surface.

In a realization of the first aspect of the present invention,

the thermoplastic resin comprises polyamide;

the inorganic material with phase change is Na2S2Q3.5H2O;

The part comprises the inorganic phase-change material on its surface.

The inorganic phase-change material can be brought into surface contact with the thermoplastic resin in part interstices, which can be interstices or grooves on the surface of the part or in chambers inside of the part manufactured for such use. If the inorganic phase change material comes into contact with the thermoplastic resin in an inner chamber of the part, the inorganic phase change material would be sealed and isolated from the external medium by the thermoplastic resin itself. If the inorganic material comes into contact with the thermoplastic resin in a groove or interstice On the surface of the part, this groove or interstice can be subsequently sealed to isolate the inorganic phase-change material from the external medium. This sealing can be carried out with different products depending on the application of the piece. For example, with petroleum jelly and/or stearic acid.

A second aspect of the present invention relates to the use of an inorganic phase-change material for the manufacture of a fatigue-resistant part consisting of a thermoplastic resin.

A third aspect of the present invention relates to a process of Obtaining the part as described above where the inorganic phase change material is in its matrix comprising the stages of:

- mixing of the thermoplastic resin with at least one inorganic material with phase change, where the inorganic material with phase change is dispersed in the polymeric matrix; y
- Forming of the part.

This forming is carried out with the usual techniques in thermoplastic resins such as thermoforming, extrusion and injection.

In a realization of the third aspect of the present invention, the procedure also has a third stage of hydrating the newly formed part in the previous stage.

A fourth aspect of the present invention relates to a process of obtaining the part as described above where the inorganic phase change material is on the surface comprising the steps of:

- Formed with the thermoplastic resin of the part, with interstices;
- filling of the interstices with at least one inorganic material with phase change;
- Sealing of the interstices.

Tai and as described above by interstice is understood interstices or grooves on the surface of the part or in chambers inside the part. If the inorganic phase change material comes into contact with the thermoplastic resin in an inner chamber of the part, the inorganic phase change material would be sealed and isolated from the external medium by the thermoplastic resin itself. If the inorganic material comes into contact with the thermoplastic resin in a groove or surface gap in the part, the groove or interstice can be subsequently sealed to isolate the phase-change inorganic material from the external medium.

In a realization of the third and fourth aspects of the present invention, the thermoplastic resin is selected from polyamide, polyoxymethylene, polyethylene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene, polyacrylonitrile-styrene-acrylate, polyvinyl chloride, polyphenylene sulphide, polymethylmethacrylate, polycarbonates, polyethylene terephthalate, polybutylene terephthalate, thermoplastic elastamers and any of their mixtures,

preferably thermoplastic resin is selected from acrylonitrile-butadiene-styrene, polyacrylonitrile, polystyrene, polyvinyl chloride, polyphenylene sulphide, polyethylene terephthalate, polymethylmethacrylate and polyamide,

Most preferably the thermoplastic resin is polyamide, and *more* preferably the thermoplastic resin is selected from polyamide 6.6, polyamide 11 and polyamide 6.10.

In a realization of the third and fourth aspects of the present invention, the thermoplastic resin is glass fiber reinforced polyamide.

In a realization of the third and fourth aspects of the present invention, the thermoplastic resin is acrylonitrile-butadiene-styrene and the material inorganic
with phase change is KAl(SQ4)2·12H2O.

In another embodiment of the third and fourth aspects of the present invention, the thermoplastic resin is polyacrylonitrile and the phase-change inorganic material is Mg(NQ3)2·6H2O.

In another realization of the third and fourth aspects of the present invention, the thermoplastic resin is polystyrene and the phase-change inorganic material is Mg(NQ3)2·6H2O.

In another embodiment of the third and fourth aspects of the present invention, the thermoplastic resin is polyvinyl chloride and the phase-change inorganic material is selected from Ba(OH)2.8H2O, Al(NQ3)2.9H2O, LiCH3CQ0.2H20 and any of their mixtures, preferably the thermoplastic resin is polyvinyl chloride and the inorganic material with phase change.
phase is Ba(OH)2.8H2O.

In another embodiment of the third and fourth aspects of the present invention, the thermoplastic resin is polyphenylene sulfide and the phase-change inorganic material is selected from Ba(OH)2.8H2O, Al(NQ3)2.9H2O, LiCH3CQO.2H2ONa3PQ4.12H2O and any of its mixtures, preferably the thermoplastic resin is polyvinyl chloride and the inorganic material with phase change is Ba(OH)2.8H2O.

In another realization of the third and fourth aspects of the present invention, the thermoplastic resin is polyethylene terephthalate and the phase-change inorganic material is selected from Na3PQ4.12H2O, NaOH.H2O, NaAl(SO4)2,10H2O, Fe(NQ3)2.2H2O, CH3CQONa.3H2O, MgCl2.4H2O, MnCl2.4H2O, Ni(NQ3)2.6H2O, FeC'3.2H2O, Zn(NQ3)2.2H2O, Ca(NQ3)2.3H2O and any of its mixtures, preferably the thermoplastic resin is polyethylene terephthalate and the inorganic material with phase change is selected from NaAl(SO4)2,10H2O, Fe(NQ3)2.2H2O and any of its blends.

In another realization of the third and fourth aspects of the present invention, the thermoplastic resin is polymethylmethacrylate and the phase-change inorganic material is selected from CH3CQONa.3H2O, MgCl2.4H2O, MnCl2.4H2O, Ni(NQ3)2.6H2O, FeC'3.2H2O, Zn(NQ3)2.2H2O, Ca(NQ3)2.3H2O, Na2S2Q3•5H2O, MgSO4.7H2O, K2HPO4.3H2O, Na2SiQ3.5H2O, Fe(NQ3)3.9H2O, Ca(NQ3).4H2O, Mg(NQ3)2.4H2O, Zn(NQ3)2.4H2O, K2HPQ4.? H2O, Cal2.6H2O, Mgl2.8H2O, KF.2H2O, CoSQ4.? H2O, Na2HPQ4.12H2O and any of their mixtures, preferably the thermoplastic resin is polymethylmethacrylate and the phase-change inorganic material is selected from Zn(NQ3)2.2H2O, Ca(NQ3)2.3H2O and any of their mixtures.

In another realization of the third and fourth aspects of the present invention, the Thermoplastic resin is polyamide 6.6 and inorganic material with change of phase is selected from Ca(NQ3)2.3H2O, MgSO4.7H2O, Na2S2Q3_5H2O, K2HPO4.3H2O, Na2SiQ3.5H2O, Fe(NQ3)3.9H2O, Ca(NQ3).4H2O, Mg(NQ3)2.4H2O,Zn(NQ3)2.4H2O, K2HPO4.7H2O, Cal2.6H2O, Mgl2.8H2O, KF.2H2O, CoSO4.7H2O, Na2HPO4.12H2O, Mn(NQ3)2.4H2O, FeCb.6H2O, Zn(NQ3)2.6H2O, LiBr2.2H2O, CaBr2.6H2O, KFe(SQ4)2.12H2O and any of its mixtures, preferably the thermoplastic resin is polyamide 6.6 and the inorganic material with phase change is selected from K2HPQ4.3H2O, Na2SiQ3.5H2O, Fe(NQ3)3.9H2O, Ca(NQ3).4H2O, Zn(NQ3)2.4H2O,

K2HPO4.7H2O and any of its mixtures, but preferably the phase-change inorganic material is Na2SiQ3.5H2O.

In another realization of the third and fourth aspects of the present invention, the thermoplastic resin is polyamide 11 and the inorganic material with phase change is selected from Cal2.6H2O, Mgl2.8H2O, KF.2H2O, Na2HPQ4.12H2O, Mn(NQ3)2.4H2O, FeCb.6H2O, Zn(NQ3)2.6H2O, LiBr2.2H2O, CaBr2.6H2O, Na2SO4.10H2O, Na2CQ3.10H2O, KFe(SQ4)2.12H2O, CoSO4.7H2O, LiNQ3.3H2O, LiNQ3.2H2O, CaCl2.12H2O, Fe8r3.6H2O, Mn(NQ3)2.6H2O and any of its mixtures, preferably the phase-change inorganic material is selected from Na2HPO4.12H2O, Mn(NQ3)2.4H2O, FeCb.6H2O, Zn(NQ3)2.6H2O and any of their mixtures.

In another realization of the third and fourth aspects of the present invention, the thermoplastic resin is polyamide 6.10 and the inorganic material with phase change is selected from Mn(NQ3)2.4H2O, FeCb.6H2O, Zn(NQ3)2.6H2O, LiBr2.2H2O, CaBr2.6H2O, KFe(SQ4)2.12H2O, Na2SO4.10H2O, Na2CO3.10H2O, LiNQ3.3H2O, LiNO3.2H2O, CaCl2.12H2O, Fe8r3.6H2O, Mn(NQ3)2.6H2O and any of its mixtures, preferably the inorganic material with change phase is selected from LiBr2.2H2O, CaBr2.6H2O, KFe(SQ4)2.12H2O, Na2SQ4.10H2O, Na2CO3.10H2O, LiNO3.3H2O, LiNQ3.2H2O and any of their mixtures.

Throughout the description and claims, the word "comprises" and Its variants are not intended to exclude other technical characteristics, additives, components or steps. For experts in the field, other objects, advantages and characteristics of the invention will follow partly from the description and partly from the practice of the invention. The following examples and figures are provided by way of illustration, and are not intended to be limited to the present invention.

DESCRIPTION OF THE FIGURES

Fig. 1.Perspective view of Example 1 part, which is a stop of the rail-sleeper fastening system of high-speed train trains. 1: thermoplastic resin part, 2: inorganic material with phase change in the interstices; L: length of the piece.

Fig. 2.Temperature evolution up to the moment of breakage; i: part of the invention; ii: part of thermoplastic resin without phase change material.

EXAMPLES

The invention will then be illustrated by tests carried out by the inventors, which highlights the improved mechanical properties of the parts of the invention.

Example 1. Procedure for obtaining a piece of the invention

At a stop of the rail-sleeper fastening system **(L=** 110 mm) (Fig. 1) of glass fibre reinforced polyamide 6.6 type E (electrical) Na2S2Q3.5H2O was incorporated on the surface, in the interstices (2) of the geometry of the part, achieving a proportion of PCM in the polymer sample of 8% by weight.

The grooves were then sealed to ensure proper tightness with a putty composed of calcium salts, petroleum jelly and stearic acid.

Example 2. Mechanical behavior of the part in Example 1

In a high-speed rail VFA fastening assembly simulator device, which has a rail clamp emulator and sleeper support,

approved by the Administrator of Railway Structures (ADIF) to carry out this type of test, according to Technical Specification, E.T. 03.360.578.3 "Light bend clamping plates". 1edition of May 1998, the part of Example 1 is fastened, so that the part is subjected to the same conditions under which their work is carried out.

Variable compression load waves between 5 and 55 kN of sinusoidal nature are applied to the workpiece at the frequency of 5 hertz with the help of a universal testing machine. Once the test has started, the evolution of the deformation due to shortening of the part by means of an inductive LVDT (*Linear Variable Differential Transformer) comparator and* the evolution of the temperature of the part is recorded simultaneously.

Figure 2 compares the thermal behaviour of a standard part free of phase change material and another equipped with phase change material, subjected to the same fatigue test. It can be seen that the standard part (ii) breaks after 35000 cycles (1.9 hours), while the PCM part (i) extends its useful life to 190000 cycles (10.5 hours) having increased his fatigue life by more than 400%. It can be seen that once the phase change temperature of the additive has been reached (which in the case of Na2S2O3.5H2O is 48.5 °C), it absorbs the heat from its environment to change its state and a cooling effect is produced on the polyamide that tends to stabilize the temperature of the component. prolonging its useful life.

DEMANDS

1.-Piece made up of a thermoplastic resin characterized by:

in its matrix and/or on its surface it comprises at least one inorganic material with phase change; y

the transition temperature of the thermoplastic resin, calculated by DSC with a heating ramp of 10°C/min in nitrogen atmosphere, is 2 to 20°C higher than the melting temperature of the inorganic material with phase change.

2.- Piece according to the previous claim, where the transition temperature of the thermoplastic resin, calculated by DSC with a heating ramp of 10°C/min in nitrogen atmosphere, is 5°C to 10°C higher than the melting temperature of the inorganic material with a change of phase.

3.- The second of any of the above claims, where the thermoplastic resin is selected from polyamide, polyoxymethylene, polyethylene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene, polyacrylonitrile Acrylonitrile-styrene-acrylate, polyvinyl chloride, polyphenylene sulphide, polymethylmethacrylate, polycarbonates, polyethylene terephthalate, polybutylene terephthalate, thermoplastic elastomers and any of their mixtures.

4.- The piece according to any of the previous claims, where the Inorganic material with phase change is a hydrate.

5.- The part according to any of the above claims, where the thermoplastic resin is acrylonitrile-butadiene-styrene and the inorganic material with phase change is KAl(SQ4)2·12H2O.

6.- The part according to any of claims 1 to 4, where the thermoplastic resin is polyacrylonitrile and the inorganic material with phase change is Mg(NQ3)2·6H2O.

7.- The part according to any of claims 1 to 4, where the thermoplastic resin is polystyrene and the inorganic material with phase change is Mg(NQ3)2·6H2O.

8.- The piece according to any of claims 1 to 4, where the resin 1Or The thermoplastic material is polyvinyl chloride and the inorganic material with phase change is selected from Ba(OH)2.8H2O, Al{NQ3)2.9H2O, LiCH3CQO.2H2O and any of its mixtures.

9.- The piece according to any of claims 1 to 4, where the resin thermoplastic is polyphenylene sulfide and the inorganic material with phase change is selected from Ba(OH)2.8H2O, Al(NQ3)2.9H2O, LiCH3CQO.2H2ONa3PQ4.12H2O and any of their mixtures.

10.- The piece according to any of claims 1 to 4, where the resin thermoplastic is polyethylene terephthalate and the inorganic material with phase change is selected from Na3PQ4.12H2O, NaOH.H2O, NaAl(SQ4)2,10H2O, Fe(NQ3)2.2H2O, CH3CQONa.3H2O, MgCl2.4H2O, MnCl2.4H2O, **Ni(NQ3}2.6H20, FeCl3.2H20, Zn(NQ3}2.2H20, Ca(NQ3)2.3H20 and any of** their mixtures.

11. The part according to any of claims 1 to 4, where the thermoplastic resin is polymethylmethacrylate and the inorganic material with phase change is selected from CH3CQONa.3H2O, MgCl2.4H2O, MnCl2.4H2O, Ni(NQ3)2.6H2O, FeCb.2H2O, Zn(NQ3)2.2H2O, Ca(NQ3)2.3H2O, Na2S2O3.5H2O, MgSO4.7H2O, K2HPO4.3H2O, Na2SiQ3.5H2O, Fe(NQ3)3.9H2O, Ca(NQ3).4H2O, Mg(NQ3)2.4H2O, Zn(NQ3)2.4H2O, K2HPO4.7H2O, Cal2.6H2O, Mgl2.8H2O, KF.2H2O, CoSO4.7H2O, Na2HPQ4.12H2O and any of their mixtures.

12. The part according to any of claims 1 to 4, where the thermoplastic resin is polyamide 6.6 and the inorganic material with phase change is selected from Ca(NQ3)2.3H2O, MgSQ4.7H2O, Na2S2Q3_5H2O, K2HPQ4.3H2O, Na2SiQ3.5H2O, Fe(NQ3)3.9H2O, Ca(NQ3).4H2O, Mg(NQ3)2.4H2O, Zn(NQ3)2.4H2O, K2HPQ4.? H2O, Cal2.6H2O, Mg'2.8H2O, KF.2H2O, CoSQ4.? H2O,Na2HPO4.12H2O, Mn(NQ3)2.4H2O, FeC'3.6H2O, Zn(NQ3)2.6H2O, Li8r2.2H2O, Ca8r2.6H2O, KFe(SQ4)2.12H2O and any of their mixtures.

13.- The part according to any of claims 1 to 4, where the thermoplastic resin is polyamide 11 and the inorganic material with phase change is selected of Cal2.6H2O, Mg'2.8H2O, KF.2H2O, CoSQ4.? H2O,Na2HPQ4.12H2O, Mn(NQ3)2.4H2O, FeC'3.6H2O, Zn(NQ3)2.6H2O, LiBr2.2H2O, Ca8r2.6H2O, Na2SQ4.10H2O, Na2CO3.10H2O, KFe(SQ4)2.12H2O, LiNO3.3H2O, LiNQ3.2H2O, CaCl2.12H2O, Fe8r3.6H2O, Mn(NQ3)2.6H2O and any of its mixtures.

14. The part according to any of claims 1 to 4, where the thermoplastic resin is polyamide 6.10 and the inorganic material is phase-change is selected from Mn(NQ3)2.4H2O, FeC'3.6H2O, Zn(NQ3)2.6H2O, LiBr2.2H2O, CaBr2.6H2O, KFe(SQ4)2.12H2O, Na2SO4.10H2O, Na2CO3.10H2O, LiNQ3.3H2O, LiNO3.2H2O, CaCl2.12H2O, Fe8r3.6H2O, Mn(NQ3)2.6H2O and
any of its mixtures.

15.- The part according to any of the above claims, where the part is selected from tape, hinge, gear, screw, fixing clip, connector and clamp.

16.- The piece according to the previous claim, where the piece is a tape in a rail-crossbeam fastening system.

17.- The part according to any of the above claims, characterized by the fact that its matrix includes the inorganic material of phase change.

18.- The part according to any of claims 1 to 16, characterized by the fact that its surface includes the inorganic material of phase change.

19.- Use of an inorganic material with phase change for the manufacture of a fatigue-resistant part made up of a thermoplastic resin.

20.- Procedure for obtaining the piece according to claims 1 to 17 which includes the stages of:
- mixing of the thermoplastic resin with at least one phase-change inorganic material, where the phase-change inorganic material is dispersed in the polymeric matrix; y
- Forming of the part.

21.- Procedure for obtaining the piece according to claims 1 to 16 and 18 which includes the stages of:
- Formed with the thermoplastic resin of the part, with interstices;
- filling of the interstices with at least one inorganic material with phase change;
- sealing of the interstices.

22.- Procedure according to any of claims 20 or 21 wherein the thermoplastic resin is selected from polyamide, polyoxymethylene, polyethylene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene, polyacrylonitrile acrylonitrile-styrene-acrylate, polyvinyl chloride, polyphenylene sulphide, polymethylmethacrylate, polycarbonates, polyethylene terephthalate, polyethylene terephthalate, polyethylene methacrylate, polyethylene methacrylate, polyethylene methacrylate, polyethylene terephthalate, polyethylene terephthalate, polyethylene methacry polybutylene, thermoplastic elasthenes and any of their mixtures.

23.- Procedure according to any of claims 20 to 22, where the glass transition temperature of the thermoplastic resin (calculated by DSC) is 2 to 20°C greater than the melting temperature of the inorganic material with phase change.

24.- Procedure according to the previous claim, where the glass transition temperature of the thermoplastic resin (calculated by DSC) is 5°C to 10°C greater than the melting temperature of the inorganic material with phase change.

25.- Procedure according to any of claims 20 to 24 where the inorganic material with phase change is a hydrate.

26.- Procedure according to any of the claims 20 to 25, where the thermoplastic resin is acrylonitrile-butadiene-styrer and the inorganic material with phase change is KAl(SQ4)2· 12H2O.

27. Procedure according to any of claims 20 to 25, wherein the thermoplastic resin is polyacrylonitrile and the inorganic material with a change of phase is Mg(NQ3)2·6H2O.

28. - Procedure according to any of claims 20 to 25, wherein the thermoplastic resin is polystyrene and the inorganic material with phase change is Mg(NQ3)2·6H2O.

29. Procedure according to any of claims 20 to 25, wherein the thermoplastic resin is polyvinyl chloride and the phase-change inorganic material is selected from Ba(OH)2.8H2O, Al(NQ3)2.9H2O, LiCH3CQO.2H2O and any of their mixtures.

30. Procedure according to any of claims 20 to 25, wherein the thermoplastic resin is polyphenylene sulphur and the inorganic material with change

of Phase It is Select of Ba(OH)2.8H2O, $Al(NO_3)_2.9H_2O$, LiCH3CQO.2H2ONa3PQ4.12H2O and any of their mixtures.

31.- Procedure according to any of the claims 20 to 25, where the thermoplastic resin is polyethylene terephthalate and the inorganic material with phase change is selected from Na3PQ4.12H2O, NaOH.H2O, NaAl(SO4)2,10H2O, Fe(NQ3)2.2H2O, CH3CQONa.3H2O, MgCl2.4H2O, MnCl2.4H2O, FeCb.2H2O, Zn(NQ3)2.2H2O, Ca(NQ3)2.3H2O and any of their mixtures.

32.- Procedure according to any of claims 20 to 25, wherein the thermoplastic resin is polymethylmethacrylate and the inorganic material with phase change is selected from CH3CQONa.3H2O, MgCl2.4H2O, MnCl2.4H2O, FeCb.2H2O, Zn(NQ3)2.2H2O, Ca(NQ3)2.3H2O, Na2S2Q3•5H2O, mgSQ4.? H2O, K2HPO4.3H2O, Na2SiQ3.5H2O, Fe(NQ3)3.9H2O, Ca(NQ3).4H2O, Mg(NQ3)2.4H2O, Zn(NQ3)2.4H2O, K2HPQ4.? H2O, Cal2.6H2O, Mgl2.8H2O, KF.2H2O, Na2HPO4.12H2O and any of their mixtures.

33.- Procedure according to any of the claims 20 to 25, where the thermoplastic resin is polyliamide 6.6 and the phase-change inorganic material is selected from Ca(NQ3)2.3H2O, MgSO4.7H2O, Na2S2Q3_5H2O, K2HPO4.3H2O, Na2SiQ3.5H2O, Fe(NQ3)3.9H2O, Ca(NQ3).4H2O, Mg(NQ3)2.4H2O, Zn(NQ3)2.4H2O, K2HPQ4.7H2O, Cal2.6H2O, Mgl2.8H2O, KF.2H2O, Na2HPO4.12H2O, Mn(NQ3)2.4H2O, FeCl3.6H2O, Zn(NQ3)2.6H2O, LiBr2.2H2O, Ca8r2.6H2O, KFe(SQ4)2.12H2O and any of their mixtures.

34. Procedure according to any of claims 20 to 25, wherein the thermoplastic resin is polyamide 11 and the inorganic material with phase change is selected from Cal2.6H2O, Mgl2.8H2O, KF.2H2O, Na2HPQ4.12H2O, Mn(NQ3)2.4H2O, FeCb.6H2O, Zn(NQ3)2.6H2O, LiBr2.2H2O, Ca8r2.6H2O, Na2SO4.10H2O, Na2CO3.10H2O, KFe(SQ4)2.12H2O, LiNQ3.3H2O,

LiNO3.2H2O, CaCl2.12H2O, Fe8r3.6H2O, Mn(NQ3)2.6H2O and any of their mixtures.

35.- Procedure according to any of the claims 20 to 25, where the thermoplastic resin is polyamide 6.10 and the inorganic material with phase change is selected from Mn(NQ3)2.4H2O, FeCl3.6H2O, Zn(NQ3)2.6H2O, Li8r2.2H2O, Ca8r2.6H2O, KFe(SQ4)2.12H2O, Na2SO4.10H2O, Na2CO3.10H2O, LiNO3.3H2O, LiNQ3.2H2O, CaCl2.12H2O, Fe8r3.6H2O, Mn(NQ3)2.6H2O and
any of its mixtures.

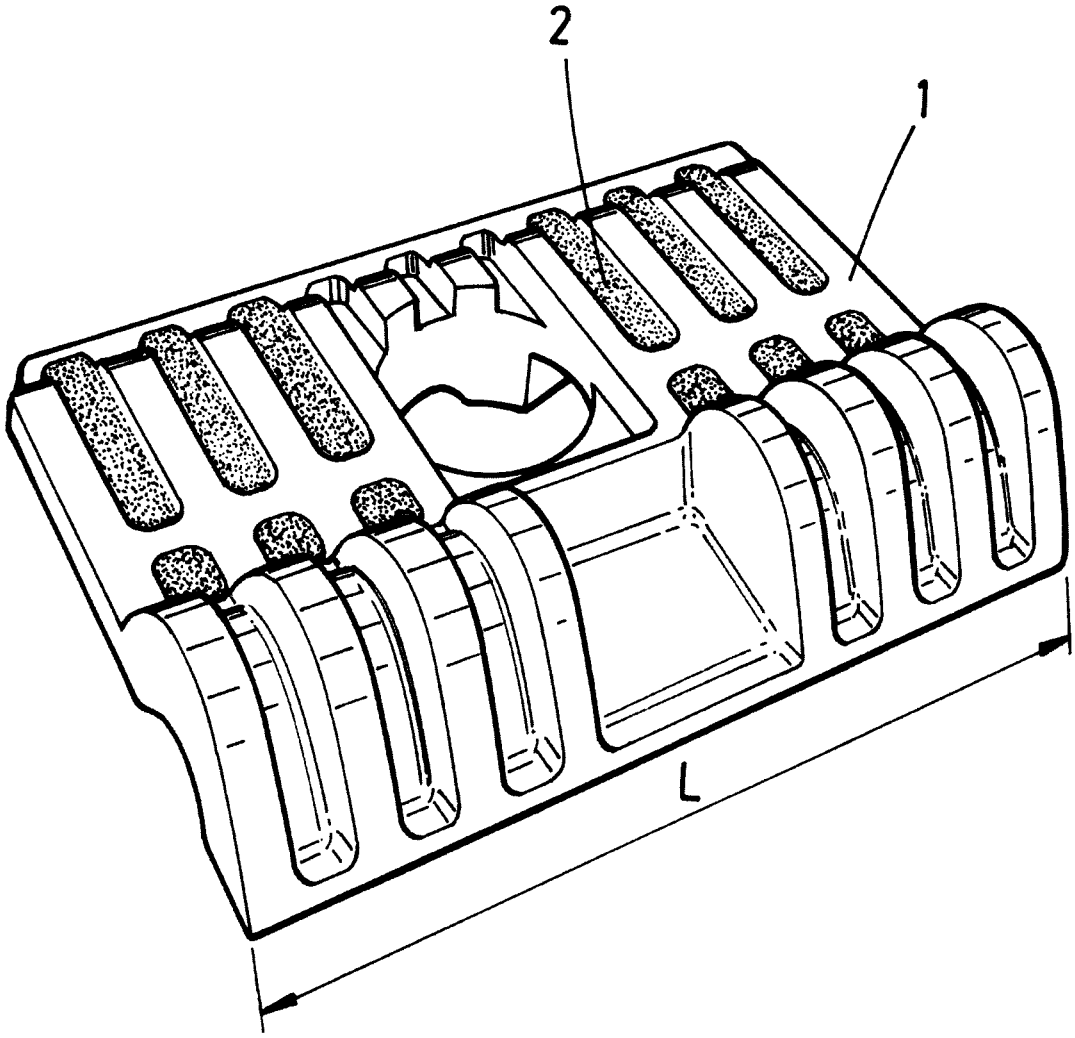
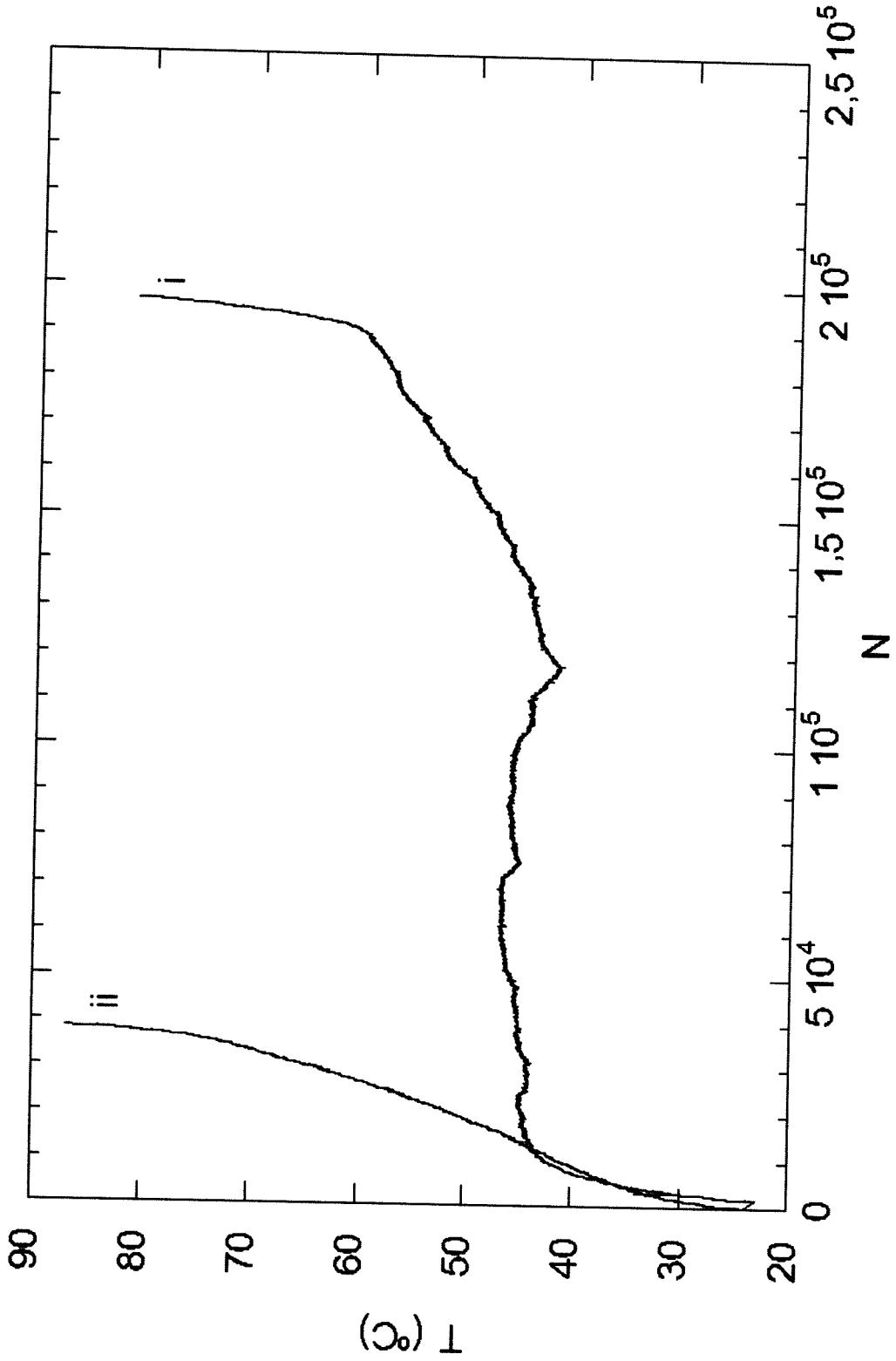


FIG.1

FIG.2



SPANISH OFFICE
PATENTS AND

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(21) Application number: 201400435

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(32) date:

REPORT ON THE STATE OF THE ART

(51) **Int. Cl. :** See Additional Sheet

RELEVANT DOCUMENTS

Category	(56) **Documents cited**	**Affected claims**
A	US 2013082116 A1 (PERRAUD ERIC ET AL.) 04/04/2013, (paras. [0001], [0033], [0070]).	1-35
A	US 3908902 A (COLLINS BENJAMIN ET AL.) 30/09/1975, column 2, lines 19-53.	1-35
A	CASADO, J.A. et al. Mechanical Behavior or Recycled Reinforced Polyamide Railway Fasteners. Polymer Composites 2010, Vol. 31, No. 7, pp. 1142-1149. See page 1142.	1-35

Category of documents cited
X: of particular relevance
And: of particular relevance combined with others of the same category
A: reflects the state of the art
Or: referred to unwritten disclosure
P: published between the priority date and the filing date
E: previous document, but published after the date of submission of the application

This report has been prepared

■ for all claims

■ for claims no:

Date of preparation of the report	**Examiner**	**Page**
26.09.2014	M. C. Bautista Sanz	1/4

CLASSIFICATION SUBJECT OF THE APPLICATION

C08L77/00 (2006.01)
C08K3/10 (2006.01)
C08K3/18 (2006.01)
E01B3/00 (2006.01)

Minimum documentation searched (ranking system followed by ranking symbols) C09K, C08K, C08L,

E01B

Electronic databases queried during the search (name of the database and, if possible, search terms used)

INVENES, EPODOC, WPI, BD full text (WO, EP, US, GB, CA, AU), HCAPLUS

Date of Written Opinion: 26.09.2014

Statement

Novelty (Art. 6.1 LP 11/1986)	Claims 1-35	**YES**
	Demands	**NO**
Inventive step (Art. 8.1 LP11/1986)	Claims 1-35	**YES**
	Demands	**NO**

The application is considered to meet the requirement of industrial application. This requirement was assessed during the formal and technical examination phase of the application (Article 31.2 of Law 11/1986).

Basis of the Opinion.-

This opinion has been made on the basis of the patent application as published.

1. Documents considered.-

The following is a list of the documents pertaining to the state of the art taken into consideration for the realization of this opinion.

Document	Publication or Identification Number	Publication Date
D01	US 2013082116 A1 (PERRAUD ERIC et al.)	04.04.2013
D02	US 3908902 A (COLLINS BENJAMIN et al.)	30.09.1975
D03	CASADO, J.A. et al. Mechanical Behavior or Recycled Reinforced Polyamide Railway Fasteners. Polymer Composites 2010, Vol. 31, No. 7, pp. 1142-1149.	2010

2. Reasoned declaration in accordance with Articles 29.6 and 29.7 of the Implementing Regulations of Law 11/1986 of 20 March 1986 on Patents on novelty and inventive step; Quotes and explanations in support of this statement

The object of the invention is a piece made up of a thermoplastic resin with an inorganic material with a phase change (inorganic salt hydrate), its use in fatigue-resistant components as well as the procedure for its preparation.

Document D01 discloses a piece of composite material of thermoplastic matrix reinforced with natural fibers for railway sleepers. The thermoplastic material used is selected among polymers and copolymers of ethylene, propylene, butylene, polyvinyl chloride, polyamide, acrylic polymers, etc. The material is processed by extrusion or injection (paragraphs [0001], [0033], [0070]).

Document D02 discloses a piece used as a railway sleeper formed by a material composed of polyester resin, wood waste and aluminum hydrate that is obtained by mixing its components and subsequent casting in a mold (column 2, lines 19-53).

Document D03 discloses parts formed from glass fibre reinforced polyamide for use in railway components. See page 1142.

None of the cited documents or any relevant combination thereof discloses or directs the person in the art to a part of a thermoplastic matrix composite material containing a phase-change inorganic material, such as that referred to in claim 1 of the application, which improves the fatigue strength of the piece of material subjected to such stresses.

Therefore, the invention defined in claims 1 to 35 meets the novelty and inventive step requirements under Articles 6.1. and 8.1. of Law 11/1986 on Patents.