

(19) World Intellectual Property  
Organization  
International Bureau

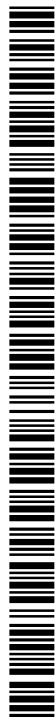


(43) International Publication Date  
30 June 2005 (30.06.2005)

PCT

(10) International Publication Number  
**WO 2005/058773 A1**

- (51) International Patent Classification<sup>7</sup>: **C04B 24/28**
- (21) International Application Number:  
PCT/US2004/042094
- (22) International Filing Date:  
16 December 2004 (16.12.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/529,750 17 December 2003 (17.12.2003) US
- (71) Applicant (for all designated States except US): **TER-RASIMCO INC.** [US/US]; 1016 Bedington Road, Martinsburg, WV 25401 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **SIMMONS, Walter, John** [US/US]; 1016 Bedington Road, Martinsburg, WV 25401 (US). **SIMMONS, Walter, Neal** [US/US]; 803 Sanderson Drive, Durham, NC 27704 (US).
- (74) Agent: **WATKINS, Seth, A.**; Steptoe & Johnson LLP, 1330 Connecticut Avenue, NW, Washington, DC 20036-1795 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
  - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 2005/058773 A1

(54) Title: TOUGHENED POLYETHYLENE TEREPHTHALATE

(57) Abstract: A composite material is disclosed having a matrix formed of polyethylene terephthalate and cement particles distributed in the matrix. The cement particles may be Portland cement. About 50 wt% or less of the composite material is cement particles. The cement particles have an average particle size of no more than about 100 µm.

## **TOUGHENED POLYETHYLENE TEREPHTHALATE**

### **FIELD OF THE INVENTION**

The invention relates to toughened polyethylene terephthalate. More particularly, the invention relates to a composite material formed of cement and recycled PET, along with a method of making same.

### **BACKGROUND OF THE INVENTION**

Waste polyethylene terephthalate (PET) polymer is neither environmentally biodegradable nor compostable, and thus suffers from disposal problems. Recycling has become a viable alternative to the long-term accumulation of garbage, and there is substantial availability of recyclable PET waste. For example, post-consumer PET derived from soft drink bottles is available in bulk for relatively low cost. Bottle-grade PET is known to be of high quality among the various PET grades, and is available particularly as washed flakes. There are major incentives from environmental perspectives and governmental regulatory directives to find new and improved uses for PET waste.

As an unreinforced, semi-crystalline thermo-plastic polyester, PET has excellent wear resistance, excellent hardness and stiffness, very good creep resistance, low coefficient of friction, high flexural modulus, and superior dimensional stability. Nevertheless, PET – particularly following melting and resolidifying of post-consumer recyclable waste – can be quite brittle and as such can be inappropriate in some applications.

U.S. Patent No. 6,583,217 B1 to Li *et al.* is directed to a composite material composed of fly ash and waste PET. Melted waste, chemically unmodified PET material and fly ash particles are mixed in a vessel to disperse fly ash particles in the melted PET material. The resulting mixture then is cooled to solidify the melted PET material to form a composite material having a matrix comprising PET and dispersoids distributed in the matrix and comprising fly ash particles.

Despite known composite materials, there exists a need for alternative PET materials with less susceptibility to brittle behavior. More particularly, there exists a need for a PET material appropriate for use in coating metals used in mechanically rigorous

applications. Also, there exists a need for a composite material formed of cement and recycled PET, along with a method of making same.

#### **SUMMARY OF THE INVENTION**

5                   The invention relates to a composite material having a matrix comprising polyethylene terephthalate and cement particles distributed in the matrix. In some embodiments, the matrix comprises chemically unmodified polyethylene terephthalate material. The cement particles may comprise, consist of, or consist essentially of Portland cement that optionally may be substantially Portland type I cement or substantially  
10 Portland type II cement. About 50 wt% or less of the composite material may be cement particles. Alternatively, about 40 wt% or less of the composite material may be cement particles. In some embodiments, about 30 wt% or less of the composite material may be cement particles, and in other embodiments about 20 wt% or less of the composite material comprises cement particles. Also, in some embodiments, about 15 wt% or less of  
15 the composite material may be cement particles.

                  About 5 wt% to about 15 wt% of the composite material may be cement particles in some embodiments, while in other embodiments about 5 wt% to about 10 wt% of the composite material may be cement particles. The cement particles may have an average particle size of no more than about 100  $\mu\text{m}$ .

20

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

                  Injection molding using melts of flakes of post-consumer PET derived from soft drink bottles has been experimentally demonstrated to produce a very brittle PET material. Such material, at a thickness of about 6 mm, has been shown to be easily  
25 breakable by hand.

                  The addition of Portland-like cements (or similar chemical compositions) to PET in the range of about 1 wt% to about 50 wt% advantageously may result in materials with enhanced mechanical behavior.

                  The chemical composition of Portland cements is generally presented  
30 below in Table I:

Table I

Component	Mass Contents(%)
CaO	58-66
SiO <sub>2</sub>	18-26
Al <sub>2</sub> O <sub>3</sub>	4-12
Fe <sub>2</sub> O <sub>3</sub> + FeO	1-6
MgO	1-3
SO <sub>3</sub>	0.5-2.5
K <sub>2</sub> O and NaO <sub>2</sub>	<1

See, e.g., Brandt, A.M., *Cement-Based Composites: Materials, Mechanical Properties and*  
 5 *Performance*. E & F Spon, 1995.

Experimentally, the addition of about 5 wt% to about 15 wt% Portland  
 cement to recycled PET has been found to greatly enhance the toughness and modulus of  
 the polymer. Filler material in the form of particulate Portland cement has been added to  
 melts of flakes of post-consumer PET derived from soft drink bottles. The Portland  
 10 cement had an average particle size of less than about 100  $\mu\text{m}$  to facilitate uniform  
 distribution, especially at higher cement levels.

Specifically, when about 5 wt% to about 15 wt% Portland type II cement  
 was added to the recycled PET flakes and melts of the PET/cement material were injection  
 molded, the final material was found to be noticeably tougher and more resilient to impact.  
 15 It was generally shown that the greater the percentage of cement, the greater the realized  
 toughness. At no more than about 15 wt%, most of the cement stuck to the surface of the  
 PET flakes resulting in a fairly homogenous melt and injection molded material.  
 However, it was shown to be difficult to add more than about 15 wt% cement to the PET  
 flakes because the cement appeared to separate from the flakes resulting in a non-  
 20 homogenous melt and injection molded material.

Also, during the experimentation, no steam or condensate was observed on  
 the mold or escaping from the ram cylinder when cement was added. From this  
 observation, it is believed that the cement acts as a getter, absorbing much of the water  
 that is on the PET flakes.

25 Additional laboratory-scale experimentation has demonstrated similar  
 toughness increases as a result of the addition of about 5 wt% to about 10 wt% Portland

type I cement to recycled PET flakes. Again, the Portland cement had an average particle size of no more than about 100  $\mu\text{m}$ . From melts of such combinations, much tougher and less brittle solid materials were produced.

The reason that Portland cement toughens PET is not well understood.

5 Three explanations for the observed toughening are proposed. First, the cement may toughen the polymer by inhibiting crack propagation. Second, the cement may act as a getter for water which is known to greatly reduce PET chain length. Third, the alkali metal in the cement may act as a weak cross-linking agent forming larger chain lengths and thus resulting in greater toughness.

10 While various descriptions of the present invention are described above, it should be understood that the various features can be used singly or in any combination thereof. Therefore, this invention is not to be limited to only the specifically preferred embodiments depicted herein.

Further, it should be understood that variations and modifications within  
15 the spirit and scope of the invention may occur to those skilled in the art to which the invention pertains. Accordingly, all expedient modifications readily attainable by one versed in the art from the disclosure set forth herein that are within the scope and spirit of the present invention are to be included as further embodiments of the present invention. The scope of the present invention is accordingly defined as set forth in the appended  
20 claims.

### The Claims

What is claimed is:

- 5                   1.       Composite material having a matrix comprising polyethylene terephthalate and cement particles distributed in the matrix.
2.       The composite material of claim 1, wherein the matrix comprises chemically unmodified polyethylene terephthalate material.
- 10                   3.       The composite material of claim 1, wherein the cement particles comprise Portland cement.
4.       The composite material of claim 3, wherein the Portland cement
- 15       substantially comprises Portland type I cement.
5.       The composite material of claim 3, wherein the Portland cement substantially comprises Portland type II cement.
- 20                   6.       The composite material of claim 1, wherein about 50 wt% or less of the composite material comprises cement particles.
7.       The composite material of claim 1, wherein about 40 wt% or less of the composite material comprises cement particles.
- 25                   8.       The composite material of claim 1, wherein about 30 wt% or less of the composite material comprises cement particles.
9.       The composite material of claim 1, wherein about 20 wt% or less of
- 30       the composite material comprises cement particles.

10. The composite material of claim 1, wherein about 15 wt% or less of the composite material comprises cement particles.

11. The composite material of claim 1, wherein about 5 wt% to about 5 15 wt% of the composite material comprises cement particles.

12. The composite material of claim 1, wherein about 5 wt% to about 10 wt% of the composite material comprises cement particles.

10 13. The composite material of claim 1, wherein the cement particles have an average particle size of no more than about 100  $\mu\text{m}$ .

14. The composite material of claim 1, wherein the polyethylene terephthalate comprises post-consumer recycled polyethylene terephthalate.  
15

15. The composite material of claim 14, wherein the cement particles comprise Portland type I cement.

16. The composite material of claim 15, wherein the cement particles 20 have an average particle size of no more than about 100  $\mu\text{m}$ .

17. The composite material of claim 14, wherein the cement particles comprise Portland type II cement.

25 18. The composite material of claim 17, wherein the cement particles have an average particle size of no more than about 100  $\mu\text{m}$ .

30

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US04/42094

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : C04B 24/28  
 US CL : 524/5

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)  
 U.S. : 524/5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
 None

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,161,915 A (HANSEN) 10 November 1992. See claims 9, 10 and 13.	1-3, 6-12, and 14
---		-----
Y		1-12, 14, 15 and 17

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search  
 28 March 2005 (28.03.2005)

Date of mailing of the international search report  
 18 APR 2005

Name and mailing address of the ISA/US  
 Mail Stop PCT, Attn: ISA/US  
 Commissioner for Patents  
 P.O. Box 1450  
 Alexandria, Virginia 22313-1450  
 Facsimile No. (703) 305-3230

Authorized officer  
 Peter Szekeley  
 Telephone No. (703) 308-0661

