

# TECHNICAL INSIGHTS

## ADVANCED MANUFACTURING TECHNOLOGY ALERT



03<sup>rd</sup> October 2014

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### **1. GRAPHENE UP AGAINST A METALLIC COMPETITOR**

Graphene consists of a flat mono layer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice. It has extraordinary electrical and mechanical properties, such as mechanical flexibility, high electrical conductivity, and chemical stability. These properties have made graphene a promising candidate for stretchable electronics. The applications of graphene are in electronics (as transistors and interconnects), detectors (as sensor elements) and thermal management (as lateral heat spreaders) .

The relentless miniaturization of electronics coupled with the invention of graphene has led the electronic materials community toward atomically thin 2D semiconductors. While graphene has lot of advantages, it lacks the band gap and thus it is not so suitable for digital electronics applications. Transition metal di-chalcogenides (TMDCs) represent one solution. TMDC compounds exhibit a wide range of electrical properties depending on poly type and the number of transition metal d-electrons and include metallic, half-metallic, semiconducting, super conducting, and charge density wave behavior.

Researchers at the Optoelectronics Research Center (ORC) of the University of Southampton have discovered a way to manufacture a material, which could be a competitor to graphene in the future. They have developed molybdenum di-sulphide ( $\text{MoS}_2$ ), a transition metal di-chalcogenides (TMDCs), which has properties that are similar to that of graphene, such as electronic conduction and mechanical strength. However, unlike graphene, the TMDCs have light-emitting properties, which can be used to manufacture photo detectors and light-emitting devices.

Talking to *Technical Insights*, Kevin Huang, who is part of the research team, said, "For graphene, there is no intrinsic band gap. Molybdenum di-sulphide has an intrinsic band gap of 1.8 eV and it can have light-emitting properties."

In the past, the techniques used for manufacturing transition metal dichalcogenides have produced only flakes of few hundred square micrometers in area.

The researchers explained that they have worked on the chalcogenide materials synthesis using chemical vapor deposition (CVD) process for the last 10 years, and their technology has now achieved fabrication of large area ultra-thin films. They said they were able to manufacture sheets of MoS<sub>2</sub> and related materials instead of just flakes.

Huang said, "We use chemical vapor deposition technology to do molybdenum di-sulphide synthesis on a large scale."

The researchers said they were working with several UK companies and universities and also the international centers at Massachusetts Institute of Technology and Nanyang Technological University.

Huang added, "This work is not patented, but we are in the process of applying for a patent."

The research work was funded by the Engineering and Physical Sciences Research Council (EPSRC) through the Center for Innovative Manufacturing in Photonics.

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## **2. NOVEL MANUFACTURING METHOD TO PRODUCE STRONG NANOCOMPOSITES**

The fabrication of strong, elastic, and hard nanocomposites is very challenging because the uniform or even distribution of nanoparticles in a metal matrix is difficult to achieve using powder metallurgy or liquid processing methods.

The researchers at the Singapore Institute of Manufacturing Technology, a research institute of A\*STAR (Agency for Science, Technology and Research) have used friction stir processing to obtain an even distribution of nano-sized aluminum oxide ( $\text{Al}_2\text{O}_3$ ) particles in aluminum. This is a new method for manufacturing nanocomposites.

A thin sheet of aluminum alloy was taken, and hundreds of 1-millimeter-diameter holes were drilled into the surface of this thin sheet. Aluminum oxide nanoparticles were injected into the holes and the sheet was heated in the oven. The sheet was allowed to cool down and then a rotating tool was plunged into it. This step is called the friction stir processing step. The friction produced between the tool and the sheet caused the material to plasticize. The tool was moved around to ensure that the entire sheet was plasticized.

The researchers explained that injection of nanoparticles before the friction stir processing step increased the concentration of nanoparticles in the composite. Also, the amount of airborne particles produced during powder placement and friction stir processing was considerably reduced.

The researchers checked the two properties that influence the strength of nanocomposites by using scanning electron microscopy. They observed that the nanoparticles were uniformly dispersed meaning that there were no weak points in the material. They also observed that the grains or the crystals of the aluminum matrix that recrystallized after being plasticized were small. The advantage of having small grains is that they can flow past each other smoothly enhancing the strength of the material.

The researchers measured the grain size before and after the friction stir processing with and without  $\text{Al}_2\text{O}_3$  nanoparticles and proved that the nanoparticles contributed to the reduction in the grain size.

The best nanoparticle distribution and the smallest grain size were obtained after passing the rotating tool through the sheet four times. They proved that the composite made in this way has improved hardness and tensile strength compared to untreated aluminum alloy sheets.

The researchers said that they are planning to continue the research to further improve the mechanical and thermal properties also the wear resistance of the nanocomposites.

Their plan is to commercialize the technology to aid the local industry. This technique has a lot of applications in car, space, and defense industries.

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### **3. TEXTURING ADDITIVE FACILITATES LARGE SCALE MANUFACTURING OF SOLAR CELLS**

Texturing of the surface is an important step in the photovoltaic (PV) manufacturing process for both monocrystalline and polycrystalline silicon wafers. Texturing removes the surface damage induced by wafer sawing. It reduces the reflectance of wafers and facilitates light trapping in the cell by creating small bumps on the surface, thus increasing cell efficiency. Monocrystalline silicon texturing is performed using an aqueous solution of KOH (potassium hydroxide) or NaOH (sodium hydroxide) with iso-propyl alcohol (IPA) or a surfactant. The anisotropic etching technique is not suitable for poly-crystalline silicon texturing.

A few years ago, mono-texturing was performed mainly using iso-propyl alcohol. IPA is not easy to control because it evaporates at the texturing temperature. Other institutes and companies have tried to develop additives for IPA application. RENA decided to develop an environmental-friendly texturing agent that will not evaporate at texturing temperature and also it will not pollute the water resources.

The researchers at IMEC, a nanoelectronics research center and RENA, a supplier for wet chemical production tools, have developed a novel isopropyl-alcohol-free process for texturing the Cz-Si wafers for manufacturing high-efficiency silicon solar cells at low cost.

In this process, instead of industrial additive iso-propyl alcohol, RENA's next generation texturing additive, monoTEX® F is used. MonoTEX F is a moderating and wetting agent that responds to changes in process temperature and alkali concentration in a linear way. The first generation of monoTEX F used two components, one for bath makeup and one for bath dosage. The latest monoTEX F is a further development as a single component solution, which has even higher productivity. The operating temperature of monoTEX F is far below its boiling point and thus the chance of wetting agent getting evaporated is ruled out, which results in stable concentration of ratios in the etching mixture during

the texturing process step. The use of monoTEX F not only simplifies the texturing process, but also widens the texturing process window, due to which more wafers can be processed in a single texturing bath.

When monoTEX F-based texturing was used to process large area PERC type solar cells, conversion efficiencies well above 21% was achieved. The main advantage is the reproducibility of low-reflectance values, AWR < 11.5%. This is one of the main factors to achieve high efficiency in mono cells.

The researchers at IMEC highlighted that monoTEX F- based texturing process can be considered for next generation high-volume manufacturing of silicon solar cells.

The reflection data from IMEC are also consistent with the mass production data. This project is funded by RENA itself.

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#### **4. PATENT ANALYSIS OF THERMOPLASTIC EXTRUSION PROCESS**

Thermoplastic extrusion is a process for converting plastic materials from solid to liquid state, thereby reconstituting them to form a finished product. The machine used for carrying out the thermoplastic extrusion process is very similar to that of an injection molding machine. It consists of a motor, which turns the thread to feed the plastic granules into a heater. In this process, the plastic fillets are gravity fed from a hopper into a jacketed screw. When the screw is made to turn about its axis, the plastic pellets are transported and pressurized. After it is pressurized, the molten material is forced through a die that converts it into a specified shape and cross section, thereby producing the parts with a wide range of length. In the extrusion process, plastics transform from a solid state into liquid and again back to solid state without the distinctive properties of the material being sacrificed, therefore, the scrap parts can be grounded and re-extruded with minimum degradation. This distinctive advantage makes this process a widespread method for reducing and recycling plastic waste. Some of the common thermoplastic materials used in this process are polystyrene, nylon, polypropylene, and polythene. These materials can be heated and then pressurized in a mold to form parts with different shapes and cross sections.

Some of the advantages of this process are that it can be used for high-volume production of parts, low cost and faster production rate in addition to providing uniform density, stable structure integrity, and products that are strong and durable.

From the patents that have been exhibited, it can be seen that the research is being carried out to improve the extrusion process (such as a co-extrusion process for co-extruding a thermoplastic elastomer, or a rounded, rectangular elastomer extrusion particle) and the materials (such as filled thermoplastic material for injection or extrusion). Such advancements would help achieve greater efficiency and higher productivity as well as enable the production of numerous sophisticated parts with greater final product quality.

Title	Publication Date/Publication Number	Assignee	Inventor	Abstract
Filled thermoplastic material suitable for injection or extrusion and corresponding production process	September 19, 2013/ WO 2013135978 A1	Algopack	Rémy LUCAS	The invention relates to a filled thermoplastic material capable of being injected or extruded, comprising at least 90% by weight, and preferably at least 97% by weight, of a mixture of a thermoplastic polyolefin, in particular of polypropylene or high-density polyethylene, with a material that forms a filler, and to the production process thereof. According to the invention, said material that forms a filler comprises an alkali metal alginate in a weight proportion of 5% to 15% of the total weight of said material, a filler agent, preferably diatomaceous earth, in a weight proportion of 65% to 80% of the total weight, a gelling agent such as calcium sulphate and a gelling control agent, and is combined with said thermoplastic polyolefin in respective weight proportions of 40 to 150 g per 100 g within said mixture.
Rounded rectangular thermoplastic elastomer (TPE) extrusion particle	July 31, 2013/ CN 203092825 U	Tianjin Jie Xiang Plastic Co., Ltd.	Peng, Jihong Xu	The utility model relates to a rounded rectangular thermoplastic elastomer (TPE) extrusion particle. The particle is of a rounded rectangular structure with four ribs provided with rounded corners, wherein the rounded rectangle is 2-4mm in rectangle length and 2-3mm in height, and the rounded corners of the four ribs are 1-2mm in diameter. According to the extrusion particle, through changing the neck mould of an extruder, the end face of the extrusion particle is of a rounded rectangle, thus enhancing the thermal stability and the weather fastness of the extrusion particle; and meanwhile, the extrusion particle is simple in structure and convenient to process, and the extrusion particle of a rounded rectangle improves the compression resistance strength of a product.
Adhesive extrusion for dynamically vulcanized thermoplastic elastomer laminates	May 22, 2013/ EP 2593287 A1	ExxonMobil Chemical Patents Inc.	Gregory S. Caraway, Porter C. Shannon, Adriana S. Silva	A coextrusion process for coextruding a thermoplastic elastomer with two outer layers of adhesive to form a film, and a laminate comprising a plurality of layers including an adhesive layer, a sublayer and a barrier layer. The barrier layer comprises a dynamically vulcanized thermoplastic elastomer composition present in one or more plies of the barrier layer. The sublayer comprises a first ply of a first adhesive composition joining the barrier layer and a second ply, and the adhesive layer comprises the second ply, which is vulcanizable with diene-based rubber. The sublayer of the adhesive can be laid down in contact with the relatively hot thermoplastic elastomer to moderate the temperature of the outer layer of the adhesive, whereby the outer layer of the adhesive at least is protected from scorching and can be co-vulcanized with rubber in a tire building process.
Polymeric drug delivery systems and thermoplastic extrusion processes for producing such systems	August 4, 2010/ EP 2211760 A1	Axia Pharmaceuticals, Llc	Stuart A. Grossman, Albert H. Owens, Wayne C. Pollock	Implants are disclosed for delivery of therapeutic agents such as opioids, and the manufacture and uses of such implants.

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Method apparatus and for of extrusion thermoplastic handrail	June 2, 2010/ EP 2190644 A1	EHC Canada, Inc.	Ronald Harold Ball, Alexander Stuart Caunce, Viqar Haider, Andrew Olivier Kenny, Douglas James Weatherall	A method and apparatus for extrusion of an article is provided. A die assembly can apply flows of thermoplastic material to an array of reinforcing cables to form a composite extrusion. A slider fabric can be bonded to one side of the composite extrusion. After exiting the die assembly, the slider fabric can act to support the extrudate as it passes along an elongate mandrel, which can cause the base of the slider fabric to change shape from a flat profile to the final internal profile of the article. The extruded article can then be cooled to solidify the material. The die can include cooling for the slider fabric and means for promoting penetration of the thermoplastic into reinforcing cables.
Thermoplastic polymer extrusion bending	May 1, 2007/ CA 2428455 C	Illinois Tool Works Inc., Arthur S. Goldman, Matthew B. Moyer	Arthur S. Goldman, Matthew B. Moyer	Methods for bending preformed thermoplastic extrusions having at least one cavity comprise filling at least one of the extrusion cavities with polymer foam and curing the foam within the filled cavity. An extrusion is heated to allow plastic deformation and then smoothly bent over a mandrill to impart a desired curved shape. Following cooling to below the extrusion's plastic deformation temperature on the mandrill, smoothly curved extrusions are removed for cooling to room temperature. Cured polymer foam within an extrusion cavity resists distortion of the cavity during the bending process.
A homogenization enhancing thermoplastic foam extrusion screw	March 9, 2005/ EP 1216125 B1	James D. Fogarty	James D. Fogarty	A foam extrusion assembly (10) having a melt region (20) and a heat extraction region (40) which extracts excess heat from a mixture of melted material pellets and blowing agent. The heat extraction region includes an elongate barrel (50) having an inlet (31) and an outlet (44), the inlet receiving the extrusion mixture for passage into the barrel wherein a heat extraction structure disposed with the barrel draws heat therefrom. An extrusion screw (60) is disposed in the barrel and includes a screw flight (64) structured to rotate within the barrel and urge the extrusion mixture towards the outlet of the barrel where a die (44) is disposed in order to form the finished product. The screw flight (64) includes a circulation channel (90) which receives quantities of the extrusion mixture upon rotation of the extrusion screw, thereby circulating the extrusion mixture towards the barrel for more effective and uniform cooling of the extrusion mixture to an extrudable temperature.



Title	Publication Date/Publication Number	Assignee	Inventor	Abstract
Thermoplastic foam extrusion assembly	July 21, 2004/ EP 1438166 A2	James D. Fogarty	James D. Fogarty	A foam extrusion assembly having a melt region which melts material pellets, an agent addition assembly which adds a foaming agent to the pellets, and a mixing assembly which mixes the pellets and the agent with one another. The mixing assembly includes an elongated barrel through which the pellets and the agent are urged from an inlet to an outlet of the barrel. The mixing assembly includes a mixing plug disposed in the barrel passages along a length thereof, the flow passages, which are structured and disposed to receive the pellets and the agent therethrough so as to define a flow path past the mixing plug, each have at least one small transverse dimension so as to restrict amounts of the pellets and the agent which enter the flow passage at one time, and are short in length as to minimize a duration of a flow restriction at the flow passages.
Fiber reinforced thermoplastic extrusion	May 8, 2002/ EP 0820848 B1	General Electric Company	Erich Otto Teutsch	The present invention relates to a process for making an extruded thermoplastic material and having continuous fiber reinforcement and a process for its preparation.
A homogenization enhancing thermoplastic foam extrusion screw	February 15, 2001/ WO 2001010617 A1	James D Fogarty	James D Fogarty	A foam extrusion assembly (10) having a melt region (20) and a heat extraction region (40) which extracts excess heat from a mixture of melted material pellets and blowing agent. The heat extraction region includes an elongate barrel (50) having an inlet (31) and an outlet (44), the inlet receiving the extrusion mixture for passage into the barrel wherein a heat extraction structure disposed with the barrel draws heat therefrom. An extrusion screw (60) is disposed in the barrel and includes a screw flight (64) structured to rotate within the barrel and urge the extrusion mixture towards the outlet of the barrel where a die (44) is disposed in order to form the finished product. The screw flight (64) includes a circulation channel (90) which receives quantities of the extrusion mixture upon rotation of the extrusion screw, thereby circulating the extrusion mixture towards the barrel for more effective and uniform cooling of the extrusion mixture to an extrudable temperature.

**Exhibit 1 depicts patents related to the thermoplastic extrusion process.**

*Picture Credit: Frost & Sullivan*

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