(54) Title: GRAPHENE BASED POLYMER COMPOSITES FOR PRODUCING CONDOMS WITH HIGH HEAT TRANSFER, IMPROVED SENSITIVITY AND CAPACITY FOR DRUG DELIVERY

(57) Abstract: A condom with higher mechanical strength, heat transfer and drug loading properties made up of graphene and its derivatives based polymer nanocomposites is provided. The graphene and its derivatives loaded with or without pharmaceutical ingredients are uniformly dispersed into Condom Making Polymers (CMPs) using dispersion methods, subsequently the condoms are produced by dip casting methods. The graphene and its derivatives are loaded with pharmaceutical active ingredients for release during intercourse to prevent sexually transmitted diseases (STD), unplanned pregnancies, and to increase the sexual pleasure.

Figure 1: Schematic diagram showing pharmaceutically active ingredients loaded graphene or its derivatives, which is uniformly dispersed into condom making polymers

A Condom making polymers
B Graphene or its derivative
Pharmaceutically active ingredients
Published:
— without international search report and to be republished upon receipt of that report (Rule 48.2(g))
GRAPHENE BASED POLYMER COMPOSITES FOR PRODUCING CONDOMS WITH HIGH HEAT TRANSFER, IMPROVED SENSITIVITY AND CAPACITY FOR DRUG DELIVERY

FIELD OF THE INVENTION:

The present invention generally relates to condoms, more specifically relates to the condoms made of graphene and its derivatives incorporated polymer nanocomposites.

BACKGROUND OF THE INVENTION:

Condoms are barrier devices used for both contraception and protection against sexually transmitted diseases (STDs) during intercourse. In recent years, incidence of STDs is increased which warrants the widespread use of condoms. Condoms are generally made of natural rubber, synthetic rubber, polyurethane, polyester, etc. Polymer composites have been used to produce a number of useful products including condoms as the polymer composites exhibit enhanced physical, chemical and mechanical properties than the host polymer. Several materials are being incorporated into polymers for producing polymer composites. Recently, graphene has attracted much attention due to its extraordinary properties.

Graphene is a crystalline form of carbon and its structure constitute a single sheet of carbon atoms bounded together with \(sp^2\) bond arranged in a honeycomb style crystal lattice. Graphene is the basic structural unit for some of the carbon allotropes such as graphite, carbon nanotubes and fullerenes. Graphene is a thinnest and transparent material which exhibits excellent mechanical strength, electrical conductivity, heat transfer property and huge surface area. In addition, Graphene Oxide (GO) is found that the planar structure and \(\pi\)-conjugated structure of GO and possibility of further functionalization endowed it with excellent ability to immobilize a large number of substance, including metals, drugs, biomolecules and fluorescent molecules.

Graphene based polymer composites are known in prior art. For example, Indian patent application Nos 1893/DELNP/2009, 2612/KOLNP/2012, 3845/CHENP/2012 and PCT publication No. 2013/127712 discuss graphene filled rubber / resin / polymer...
nanocomposites. Zahn et al. (J. Mater. Chem., 2012, 22, 10464) produced vulcanized graphene/natural rubber composites with a conductive segregated network exhibiting good electrical conductivity, water vapor permeability and high mechanical strength by self-assembly in latex and static hot pressing. However, there is no use of graphene on condom making.

PCT publication No. 2012/099853 discloses an elastomeric composition for producing elastomeric article such as condoms, gloves etc. and the elastomeric article includes at least one coating. Additives of high thermal conductivity such as metal particulates, graphenes, nanocarbon tubes etc. can also be used as coatings. But it does not disclose graphene incorporated polymer composite for making condoms.

Many existing patents and applications disclose condoms containing carbon allotropes such as graphite, fullerenes and carbon nanotubes. For example, US patent application No. 2005/0152891 relates to polymer entrained carbon nanotubes, where the nanotubes contain nitric oxide or a gas for delivering nitric oxide to the treatment site which is at the risk of clot formation such as in the area of an implanted stent. Russian document 2128484 discloses a condom comprising fullerenes as fillers.

US patent application No 2013/0150943 relates to a biodegradable implantable device comprising biodegradable polymer. The strength and toughness of the polymeric material is enhanced by incorporating additives such as carbon nanotubes into the polymeric material.

German document 3705293 discloses a contraceptive device which is made up of rubber or similar material. The device also contains electrical conducting material such as carbon, graphite for overcoming insulating characteristics of the rubber material.

China document 202154785 discloses a penis-like series condom which is made of a novel adhesive elastic material which contains randomly connected carbon nanotubes.

US patent application No 2001/0053813 describes a rubber composition comprising crosslinked rubber particles, silica and graphite. The rubber composition can be converted into a vulcanized rubber having excellent tensile strength and wearing resistance to make sanitary material such as a contraceptive rubber.
PCT publication No. 1995/021637 relates to condom with anti-viral properties made of Langmuir-Blodgett fullerene coated latex rubber.

US patent No. 6355350 discloses with biocompatible carbonaceous films and method for fabricating such films on medical implantation. The carbonaceous film coating can be applied to contraceptive spirals.

Taiwan document 296519 explains a method of producing sanitary delight nano-condom by mixing appropriate amount nanopowders of elemental carbon, metal, metal oxide, ceramics, mineral in particle diameter (smaller than 1000 nm) with rubber material.

Though these prior art discuss condoms made of polymer incorporated with carbon allotropes like graphite, carbon nanotubes and fullerenes having improved mechanical and/or heat conducting properties, none of them discloses the use of graphene and its derivatives which has superior qualities over other carbon allotropes in Condom Making Polymers (CMPs).

Hence, there is a need for next generation condoms (a multipurpose preventive device) made of graphene based polymer composites with higher mechanical, heat conducting and drug loading properties.

**SUMMARY OF THE INVENTION:**

The present invention provides a condom made up of graphene based polymer nanocomposites. The graphene and its derivatives are incorporated into condom making polymers (CMPs) such as natural rubber, synthetic rubber, polyurethane, polyester etc. to produce thinner condom of ≤ 0.04 mm thickness with superior mechanical, heat conductive and drug loading properties.

The method of incorporating graphene and its derivatives loaded with or without pharmaceutical active ingredients into Condom Making Polymers (CMPs) include (a) Non-covalent dispersion method (b) Covalent dispersion method. The non-covalent dispersion
method includes high shear force / in situ polymerization and the covalent dispersion method include polymer or oligomer grafting / functionalization of graphene and its derivatives.

In preferred embodiment of the invention, pharmaceutical active ingredients which include antiretroviral drug / spermicide / vasodilators / flavors are loaded into graphene and its derivatives for release during intercourse to prevent sexually transmitted diseases (STDs), unplanned pregnancies and to increase the sexual pleasure.

**BRIEF DESCRIPTION OF THE DRAWINGS:**

The objective of the present invention will now be described in more detail with reference to the accompanying drawing, in which:

Fig. 1 is a schematic diagram showing pharmaceutically active ingredients loaded graphene and its derivatives, which is uniformly dispersed into condom making polymers (CMPs).

**DETAILED DESCRIPTION OF THE INVENTION:**

The present invention discloses a condom as shown in Fig. 1 made up of pharmaceutically active ingredients loaded graphene and its derivatives based polymer nanocomposites.

According to the present invention, the graphene and its derivatives are incorporated into condom making polymers such as natural rubber, synthetic rubber, polyurethane, polyester etc. to produce thinner condom of ≤ 0.04 mm thickness with superior mechanical, heat conductive and drug loading properties. The graphene derivatives include Graphene oxide (GO), GO ammonia and functionalized graphene (GO and its derivatives).

The method of incorporating graphene and its derivatives loaded with or without pharmaceutical active ingredients into Condom Making Polymer (CMPs) includes (a) Non-covalent dispersion method (b) Covalent dispersion method.
Non-covalent dispersion method of the present invention uses any one of the following two methods for dispersing graphene and its derivatives into Condom Making Polymer (CMP). The method includes (1) High shear force (2) In situ polymerization.

Embodiments of the invention will be described by way of example.

In one embodiment of the present invention, non-covalent dispersion method using High shear force: Graphene or Graphene derivatives such as Graphene oxide (GO) or GO ammonia or functionalized GO is uniformly dispersed into the Condom Making Polymers (CMPs) using high shear devices such as ultra sound and high pressure homogenizer. After uniform dispersion into condom making polymers (CMPs), GO or its derivatives is reduced using reducing agents such as hydrazine monohydrate or sodium borohydride or environmentally friendly reducing agents such as tryptophan, ascorbic acid etc., using the same high shear devices.

Two different processing methods were used to incorporate reduced GO and graphene into CMP and are given below.

Example 1

Process to incorporate reduced rGO: The current process provides us with a new product and new method for the manufacture of reduced graphene oxide (rGO) incorporated male condoms from natural rubber latex.

Commercially available graphite powder is mixed with 98 % sulphuric acid (1:17.5) in a 500 ml beaker for about 2-5 hrs. Potassium permanganate is gradually added (1:3 ratio with respect to graphite) to the above solution (10 - 40 min interval time used). The temperature should always be below 10 - 20°C. The mixture is then stirred at 30 - 40 °C for 4-5 hrs. The resulting solution is then diluted by adding 80 -100 mL of water under vigorous stirring and a dark brown suspension is obtained. The suspension was then treated by adding 30% hydrogen peroxide solution (5 -10 ml) and 100-200 mL of distilled water. The resulting graphite oxide suspension was washed by repeated centrifugation with 5 % HCl followed by distilled water until the pH of the solution becomes neutral (centrifugation speed 5000 - 10000 rpm for 5-20
mins). The GO nanostructure are then obtained by adding 100-200 mL of water to the resulting precipitate and then bath sonicated (5 - 10 mins) to attain a uniform suspension of GO.

The GO suspension is then mixed with compounded latex to prepare the rGO incorporated Natural Rubber latex condoms with varying rGO content (0.1 to 20 phr). GO suspension is mixed with compounded latex and the whole mixture is probe sonicated (30 to 90% amplitude) to obtain uniform dispersion of GO in NR latex (sonication time varying from 1-10 mins). To this mixture one of the following reducing agents such as hydrazine hydrate/trypotaphan/ascorbic acid/urea/thiourea-ammonia/enzymes etc. is added to obtain the rGO incorporated NR latex. rGO incorporated NR latex condoms are then prepared by dip casting on to glass moulds (speed of the machine adjusted to obtain suitable thickness). The number of dipping can also be varied depending on the thickness required. The dipped samples are then vulcanised at 60 - 100 °C in a hot air oven and then stripped from the glass moulds using silica powder to obtain the rGO incorporated NR latex condoms.

rGO incorporated NR latex condoms showed a 50-100 % increase in mechanical properties on increasing the rGO content from 0.1 phr to 20 phr. The thermal conductivity of the samples was also increased by 50-100 %.

Example 2

**Process to incorporate graphene:** The current method provides us with a new product and new process for the manufacture of graphene incorporated male condoms from natural rubber latex.

The present investigation concentrates on the exfoliation of graphite to graphene using planetary ball milling in presence of melamine or other suitable exfoliating agents (Ester Vazquez et al. ACS Nano, 2014, 8 (1), pp 563-571). Commercially available graphite is mixed with melamine/curcuminoids/tetrahydrocurcuminoids/triazine derivatives (ratio varying from 1:0.5 to 1:10 graphite and exfoliating agent) in a planetary ball mill with varying milling speed (100-250 rpm) and time (1-3 hrs). The dry milled sample is then dispersed in water or DMF to obtain few layers of graphene. The exfoliated graphene is then
characterized by means of XRD, Raman spectroscopy, TEM and AFM analysis. The dispersion can be further stabilized by means of probe sonication process.

The graphene dispersion is then mixed with compounded latex to prepare the graphene incorporated NR latex condoms with varying graphene content (0.1 to 20 phr). Graphene dispersion after probe sonication is mixed with compounded latex and the whole mixture is probe sonicated again to obtain uniform dispersion of graphene in NR latex (sonication time varying from 1-10 mins). Graphene incorporated NR latex condoms are then prepared by dip casting on to glass moulds (speed of the machine adjusted to obtain suitable thickness). The number of dipping can also be varied depending on the thickness required. The dipped samples are then vulcanised at 60 - 100 °C in a hot air oven and then stripped from the glass moulds using silica powder to obtain the graphene incorporated NR latex condoms.

Graphene incorporated NR latex condoms showed a 50-100 % increase in mechanical properties on increasing the graphene content from 0.1 phr to 20 phr. The thermal conductivity of the samples was also increased by 50-100 %.

In another embodiment of the present invention, ηηη-covalent dispersion method using in situ polymerization: GO or its derivatives is dissolved into the monomers particularly isoprene in order to prepare emulsion. Further the emulsion is polymerized. During the product formation, Graphene Oxide (GO) is reduced using reducing agents such as hydrazine monohydrate or sodium borohydride or environmentally friendly reducing agents such as tryptophan, ascorbic acid etc.,

Example 3

The total solid content of the reaction mixture to 10-40% by mixing 7.5-30% weight of isoprene, graphene oxide 0.5- 2% and 2-8% vinyl carbazole in water. Then the surfactant (SDS-7% of total reaction) and the stabiliser (hexadecane-5% of monomer solution) are mixed into the system using magnetic stirring until homogeneous system is obtained. Then the reaction solution was purged for 10 minutes by N₂ gas to ensure complete removal of air from the reaction mixture.
The miniemulsion was then prepared by continuous probe sonication for 2 minutes. After sonication the reaction is initiated by the use of initiator (potassium persulphate/benzoyl peroxide - 0-2% of monomer weight). After the addition of initiator, the whole reaction mixture was kept at room temperature under N\textsubscript{2} atm for 4-5 hrs. The reaction progress was monitored using kinetic studies. The above mixture is then mixed with compounded latex, graphene oxide is then reduced by adding suitable reducing agents like ascorbic acid/hydrazine hydrate/thiourea dioxide-NH\textsubscript{3}/urea to prepare the rGO incorporated NR latex condoms with varying rGO content (0.1 to 20 phr). rGO dispersion after sonication is mixed with compounded latex and the whole mixture is sonicated again to obtain uniform dispersion of rGO in NR latex (sonication time varying from 1-10 mins). rGO incorporated NR latex condoms are then prepared by dip casting on to glass moulds (speed of the machine adjusted to obtain suitable thickness). The number of dipping can also be varied depending on the thickness required. The dipped samples are then vulcanised at 60 - 100 °C in a hot air oven and then stripped from the glass moulds using silica powder to obtain the rGO incorporated NR latex condoms.

rGO incorporated NR latex condoms showed a 20-50 % increase in mechanical properties on increasing the rGO content from 0.1 phr to 20 phr. The thermal conductivity of the samples was also increased by 20-50 %.

Covalent dispersion method of the present invention uses any one of the following two methods for dispersing graphene and its derivatives into Condom Making Polymers (CMPs). The methods include (1) Polymer or Oligomer grafting (2) Functionalization of GO or its derivatives.

In a further embodiment of the present invention, covalent dispersion method by Polymer or Oligomer grafting: Condom Making Polymers (CMPs) or its oligomers are grafted into GO and its derivatives by either grafting to or grafting from approach. Grafting from approach involves performing controlled radical polymerization initiators that is covalently attached via esterification/amidation with the carboxylic acids/alcohols/amines present across in GO platelet surface. Grafting to approach includes first to produce alkyne/amine end functionalized CMPs and to graft with azide functionalized GO by Cul catalyzed azide-alkyne cycloaddition/carbodiimide coupling.
Example 4

A. Grafting to approach

**Step 1:** The atom transfer radical polymerization (ATRP) initiator, Propargyl 2-bromoisobutyrate (PgBiB), was synthesized as per the protocol available in the literature (1. N. V. Tsarevsky, B. S. Sumerlin, K. Matyjaszewski, Macromolecules 2005, 38, 3558. 2. L. Ragupathy, D. G. Millar, N, Tirelli, F. Cellesi, Macromolecular Bioscience 2014.) The produced ATRP initiator (1-3 mmol) is mixed with isoperene monomer (30-50 mmol) in a parallel reactor tube. The mixture is first degassed by nitrogen purging for 30 min. THF (HPLC grade, 5-10 ml) is then added to the reaction mixture and stirred for few mins. The copper catalyst (Cu(I)Cl; 1-1.5/0.5-1/0.1-0.5 mmol) and bipyridine ligand (2-2.5/1-1.5/0.5-1 mmol) is then quickly added to the reaction mixture. The reaction mixture is then magnetically stirred for 4 h at around 40-60 °C. Polymerization can be terminated by dilution with aerated THF. The reaction mixture will turn from brown to blue green indicating aerial oxidation of Cu (I) to Cu (II). The copper catalyst can be removed by passing through silica gel column. The solvent can be removed under reduced pressure to obtain the oligomer or polymer.

**Step 2:** Graphene oxide is reacted with 11-azido-3,6,9-trioxaundecan-1-amine (1:1 - 1:5) in water/DMF medium using EDC coupling mechanism. 100 mL graphene oxide dispersion (1 mg/mL) is prepared in DMF or water by sonicating in bath sonicator for 1.5 h. After each 15 minutes the water in bath sonicator is replaced to reduce the heat produced. The above mentioned GO dispersion is taken in an RB flask and then 30-50 mmol N-hydroxy succinimide (NHS) is added followed by the addition of 30-50 mmol 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) under N₂ atmosphere and ice cold condition. To this reaction mixture 0.3-0.5 M NaHCO₃ [0.3 M] is added to neutralize the hydrochloride. The reaction is kept stirring under ice cold condition for 2-4 h. After two hours, to this reaction mixture 15-20 mmol 11-azido-3,6,9-trioxaundecan-1-amine is added and the reaction mixture is kept stirring at room temperature for 24 h.

**Step 3:** The products obtained from step 1 and step 2 are coupled using Azide-Alkyne Huisgen click reaction. 1:1 to 1:5 wt% of products from step 1 and 2, respectively, were
taken in DMF or water. The reaction mixture was purged with Argon for 5 min. Then, the ligand hexamethyl-triethylene tetraamine and catalyst CuBr (1 equiv. relative to -C≡CF), were added to the reaction mixture and stirred at room temperature for 24 h. Afterwards, the reaction mixture was centrifuged with excess of water to obtain the final product.

Example 5

B. Grafting from approach

Step 1: GO-ATRP initiator has been produced by adopting the reported literature. 15-20 mmol 2-bromoisobutyricacid is dissolved in 50 mL of DMF. Then, 30-50 mmol N-hydroxy succinimide (NHS) is added followed by the addition of 30-50 mmol 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) under N₂ atmosphere and ice cold condition. To this reaction mixture 0.3-0.5 M NaHCO₃ is added to neutralize the reaction mixture. Afterwards, 10-100 mL graphene oxide dispersion (1 mg/mL) is prepared in DMF or water by sonicating in bath sonicator for 1.5 h. The above mentioned GO dispersion is added into this reaction mixture and kept stirring at room temperature for 24 h. Afterwards, the reaction mixture was centrifuged with excess of water to obtain the final product.

Step 2: The above obtained product is then made to undergo ATRP reaction with isoprene in THF using the protocol given above (Grafting from approach step 1).

The obtained products from grafting from and grafting to approach are then added to compounded NR latex with varying content (0.3 - 5 phr) to obtain the final condom product. The mechanical properties and thermal conductivity is tested based on the variation in phr content of graphene or its derivatives.

The obtained products from grafting from and grafting to approach showed a 20-50 % increase in mechanical properties on increasing the rGO content from 0.1 phr to 20 phr. The thermal conductivity of the samples was also increased by 30-60 %.

In a further embodiment of the present invention, covalent dispersion method by Functionalization of GO or its derivatives: Functionalizing GO and its derivatives with
acrylic anhydride/acryloyl chloride followed by mixing and crosslinking with Condom Making Polymers (CMPs) during condom manufacturing process.

Example 6

100 mL of GO in DMF (1 mg/mL) and thiethylamine (1:2 wt%) was taken into a round bottom flask and stirred at ice cold temperature. Then, 5 to 20 wt% of acyloyl chloride was added to the reaction mixture slowly and stirred at room temperature for 24 h. Then, this mixture was centrifuged with excess amount of water to obtain the final product, which is again reduced using the same above mentioned reducing agents. Different amounts of acrylated rGO (0.3-10 phr) were added into the latex to produce the condoms.

The obtained condoms from acrylation of GO and followed by incorporation into latex shows a 20-50 % increase in mechanical properties on increasing the rGO content from 0.1 phr to 20 phr. The thermal conductivity of the samples was also increased by 30-60 %

In preferred embodiment of the invention, incorporation of pharmaceutical ingredients into condoms: pharmaceutical ingredients which include antiretroviral drugs / spermicides / vasodilators / flavors are loaded into Graphene and its derivatives for release during intercourse to prevent sexually transmitted diseases (STDs), unplanned pregnancies and to increase the sexual pleasure.

Example 7

According to the present invention, the antiretroviral drugs (i.e) Dapivirine or Tenofovir or Curcumin and spermicide Nonoxynol-9 are loaded into Graphene, GO and functionalized GOs by dissolving antiretroviral drugs and spermicide in DMSO/DMA/DMF with Graphene, GO or functionalized GOs in water solution. The excess, unloaded drugs precipitated are removed by centrifugation. Alternatively, the antiretroviral drugs and spermicide are loaded into Graphene, GO and functionalized GOs by sonication at pH > 6 for 0.5 h followed by stirring overnight at room temperature. All samples are adjusted to pH <6 with 1 M hydrochloride and then ultracentrifuged at 14000 rpm for 1 h. Finally, the drug loaded Graphene, GO and its derivatives are uniformly dispersed into the condom making polymers
using any one of the above mentioned dispersion methods. The uniformly dispersed nanomaterial also forms a network during the optimized processing conditions.

Example 8

Small pieces (2cm x 2cm) of the above said drugs loaded condoms were placed in a vaginal simulated liquid (10 ml) in a shaker at 37 °C. Small amount of sample was withdrawn after (2, 5, 10, 30 and 60 minutes) for HPLC analysis to calculate the amount of drug released.

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.
We claim,

1. A polymeric nanocomposite condom comprising;
   (a) at least one condom making polymer,
   (b) graphene or its derivatives incorporated into said condom making polymer, and
   (c) at least one pharmaceutically active ingredient loaded in said graphene or said nanocomposite
   where the said polymeric nanocomposite provides higher mechanical strength, heat transfer, drug loading properties and ≤ 0.04 mm thickness.

2. A non-covalent dispersion method based condom manufacturing process where reduced graphene oxide is incorporated into the CMPs by using high shear devices comprising the steps of:
   (a) mixing GO suspension with compounded latex and the whole mixture is probe sonicated to obtain uniform dispersion of GO in NR latex,
   (b) adding reducing agents to the above mixture to obtain the rGO incorporated NR latex,
   (c) preparing rGO incorporated NR latex condoms by dip casting on to glass moulds, where the speed of the machine and the number of dippings can be varied to obtain the required thickness,
   where the rGO incorporated NR latex condoms showed a 50-100 % increase in mechanical properties on increasing the rGO content from 0.1 phr to 20 phr,
   where the thermal conductivity of the samples were also increased by 50-100 %.

3. A non-covalent dispersion method based condom manufacturing process where graphene is incorporated into the CMPs by using high shear devices comprising the steps of:
   (a) exfoliating graphite to graphene using planetary ball milling in presence of melamine or other suitable exfoliating agents,
(b) dispersing the dry milled sample in water or DMF to obtain few layers of graphene,

(c) mixing graphene dispersion with compounded latex and the whole mixture is probe sonicated to obtain uniform dispersion of graphene in NR latex,

(d) preparing graphene incorporated NR latex condoms by dip casting on to glass moulds, where the speed of the machine and the number of dippings can be varied to obtain the required thickness,

where the graphene incorporated NR latex condoms showed a 50-100% increase in mechanical properties on increasing the graphene content from 0.1 phr to 20 phr,

where the thermal conductivity of the samples were also increased by 50-100%.

4. A non-covalent dispersion method based condom manufacturing process by in situ polymerisation where GO or its derivatives is dissolved into the monomers particularly isoprene in order to prepare emulsion, polymerising the emulsion and reducing the GO using reducing agents comprising the steps of:

(a) mixing 7.5-30% weight of isoprene, graphene oxide 0.5-2% and 2-8% vinyl carbazole in water to obtain total solid content of the reaction mixture to 10-40%,

(b) preparing a miniemulsion by continuous probe sonication of the above mixture,

(c) initiating the reaction in the above mixture by the use of an initiator, where the initiators are potassium persulphate or benzoyl peroxide,

(d) mixing the above mixture with compounded latex,

(e) reducing the graphene oxide by adding suitable reducing agents,

(f) mixing rGO dispersion after sonication with compounded latex and the whole mixture is sonicated again to obtain uniform dispersion of rGO in NR latex,

(g) preparing rGO incorporated NR latex condoms by dip casting on to glass moulds, where the speed of the machine and the number of dippings can be varied to obtain the required thickness,

where the rGO incorporated NR latex condoms showed a 20-50% increase in mechanical properties on increasing the rGO content from 0.1 phr to 20 phr,

where the thermal conductivity of the samples were also increased by 20-50%. 


A covalent dispersion method based condom manufacturing process by polymer (CMPs) or oligomer grafting by grafting to approach which includes first to produce alkyne or amine end functionalized CMPs and to graft with azide functionalized GO by Cul catalyzed azide-alkyne cycloaddition or carbodiimide coupling comprising the steps of:

- (a) reacting Graphene oxide with 11-azido-3,6,9-trioxaundecan-1-amine (1:1 - 1:5) in water/DMF medium using EDC coupling mechanism,
- (b) coupling the polymer or the oligomer with the product obtained from step (a) using Azide-Alkyne Huisgen click reaction

where the reaction mixture was centrifuged with excess of water to obtain the final product,

where the obtained product is added to compounded NR latex with varying content (0.3 - 5 phr) to obtain the final condom product,

where the products from grafting to approach showed 20-50% increase in mechanical properties on increasing the rGO content from 0.1 phr to 20 phr.

6. A process according to claim 5, where the oligomer or polymer (CMPs) for grafting to approach is obtained by performing ATRP to produce acetylene terminated isoprene oligomer/polymer using copper catalyst and bipyridine ligand in THF.

7. A covalent dispersion method based condom manufacturing process by polymer (CMPs) or oligomer grafting by grafting from approach which involves performing controlled radical polymerization initiators that is covalently attached via esterification or amidation with the carboxylic acids, alcohols or amines present across in GO platelet surface comprising the steps of:

- (a) synthesizing GO-ATRP initiator,
- (b) dissolving 2-bromoisobutyricacid in DMF, followed by addition of N-hydroxy succinimide and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) under N₂ atmosphere and ice cold condition,
- (c) adding the GO dispersion into the above reaction mixture and kept stirring at room temperature,
- (d) obtained product is then made to undergo ATRP reaction with isoprene in THF using the protocol of step (a),
where the obtained product is added to compounded NR latex with varying content (0.3 - 5 phr) to obtain the final condom product,

where the products from grafting from approach showed 20-50 % increase in mechanical properties on increasing the rGO content from 0.1 phr to 20 phr.

8. A covalent dispersion method based condom manufacturing process by functionalizing GO and its derivatives with acrylic anhydride/acryloyl chloride followed by mixing and crosslinking with condom making polymers comprising the steps of:

(a) stirring GO in DMF and tiethylamine at ice cold temperature and followed by the addition of acyloyl chloride/acrylic anhydride to the reaction mixture,

(b) adding different amounts of acrylated rGO (0.3-10 phr) into the latex to produce the condoms,

where the obtained condoms from acylation of GO and followed by incorporation into latex shows a 20-50 % increase in mechanical properties on increasing the rGO content from 0.1 phr to 20 phr,

where the thermal conductivity of the samples were also increased by 30-60 %.

9. A method of incorporation of pharmaceutical ingredients into condoms comprising; loading drugs into Graphene, GO and functionalized GOs by dissolving the said drugs in DMSO/DMA/DMF with GO or functionalized GOs in water/methanol/DMF solution, where the drug loaded Graphene, GO and its derivatives are uniformly dispersed into the condom making polymers using dispersion methods.

10. A method of incorporation of pharmaceutical ingredients into condoms comprising the steps of:

(a) loading drugs into Graphene, GO and functionalized GOs by sonication at pH > 6 for 0.5 h followed by stirring overnight at room temperature,

(b) adjusting the samples to pH <6 with 1 M hydrochloride and then ultracentrifuged at 14000 rpm for 1 h,

where the drug loaded Graphene, GO and its derivatives are uniformly dispersed into the condom making polymers using dispersion methods.
11. A condom made up of graphene and its derivatives based polymer nanocomposites, said polymer nanocomposite provides higher mechanical strength, heat transfer and drug loading properties to said condom.

12. A condom according to claim 11, wherein said condom has reduced thickness of \( \leq 0.04 \) mm.

13. A condom according to claim 11, wherein said polymer is selected from natural rubber, synthetic rubber, polyurethane and polyester.

14. A condom according to claim 11, wherein said graphene derivatives include Graphene, Graphene Oxide, GO ammonia, polymer/oligomer/acrylate functionalized GO.


16. A condom prepared according to claim 15, wherein said graphene and its derivatives are loaded with pharmaceutical active ingredients.

17. A condom prepared according to claim 15, wherein said graphene and its derivatives are not loaded with pharmaceutical active ingredients.

18. A condom prepared according to claim 15, wherein said dispersion method comprises at least one of non-covalent dispersion method and covalent dispersion method.

19. A condom prepared according to claim 18, wherein said non-covalent dispersion method comprises at least one of high shear force method and in situ polymerization method.
20. A condom prepared according to claim 18, wherein said covalent dispersion method comprises at least one of polymer or oligomer grafting and functionalization of GO and its derivatives method.

21. A condom prepared according to claim 16, wherein said pharmaceutical active ingredients comprise at least one of antiretroviral drug, spermicide, flavors and vasodilators.

22. A condom prepared according to claim 21, wherein said antiretroviral drug is selected from Dapivirine, Tenofovir, Curcumin.

23. A condom prepared according to claim 21, wherein said spermicide is Nonoxynol-9.
Drawings

Figure 1: Schematic diagram showing pharmaceutically active ingredients loaded graphene or its derivatives, which is uniformly dispersed into condom making polymers.

A Condom making polymers
B Graphene or its derivatives
+ Pharmaceutically active ingredients