FINAL REPORT

1. Project Title: **"Investigation on structure-property relationship for self-healing smart hyperbranced polyurethane nanocomposite with antistatic and antimicrobial attributes"**	SERB No: **EMR/2016/001598, dated 04 January, 2017**
2. PI (Name & Address): Prof. Niranjan Karak	Date of Birth: 21.02.1968
3. Co-PI (Name & Address): Prof. A. K. Kumar	Date of Birth: 01.02.1964

4. Broad area of Research: Chemical Sciences

4.1 Sub Area: Inorganic & Physical Chemistry

5. Approved Objectives of the Proposal :

The main objective of the present project is to investigate the structure-property relationship of efficient repeatable self-healing smart hyperbranched polyurethane/graphene-nanohybrid nanocomposites with antistatic and antimicrobial attributes for multifaceted advanced applications.

The main objective is associated with following sub-objectives.

i) To prepare hyperbranched polyurethanes with varieties of structures by the conventional technique.
ii) To prepare and functionalize graphene based nanohybrids with different nanomaterials by facile methods.
iii) To fabricate hyperbranched polyurethane nanocomposites at different dose levels of the above nanohybrids, separately and in combination.
iv) To characterize above prepared polyurethanes, nanohybrids and nanocomposites by different spectroscopic and analytical techniques.
iv) To evaluate the performance characteristics of the above pristine matrix, bare nanohybrid and nanocomposites as self-healing smart materials with antistatic and antimicrobial attributes.
v) To determine the healing efficiency by the measurement of the recovery with respect to its initial to post-damage state as the ratio of fracture stress before ($\sigma_{initial}$) and after healing (σ_{healed}).
vii) To investigate the structure-property relationship the studied polymeric materials to design the best performing self-healing smart material with antimicrobial and antistatic properties.

Date of Start: 25.01.2017	Total cost of Project: **Rs. 29,93,518.00**
Date of completion:24.01.2020	Expenditure as on: 14/01/2020 **Rs. 27,61,779/-**

6. Methodology :

To fulfill the objectives of the proposed project the entire research work is divided in two different parts. The approaches for the present proposed project are as follows.

a) Administrative

The chemicals and glass wares sanctioned in the project were procured.

b) *Technical works*

i) Bio-based smart hyperbranched polyurethane (HBPU) was prepared by using vegetable oil based resources and characterized by FT-IR, NMR and XRD.

ii) Bio-based HBPU was modified by using PDMS and characterized by FT-IR, NMR, XRD and SEM.

iii) PDMS modified PU was further modified using different amount (weight%) of cashew nut shell liquid (CNSL).

iv) An interpenetrating polymer network (IPN) was synthesized using PDMS modified HBPU and polystyrene and characterized by FT-IR, NMR, XRD and SEM.

v) Obtained IPN was further modified by using different weight% of polystyrene-grafted-MWCNT (PS-g-MWCNT). Modified PS-g-MWCNT and the fabricated nanocomposites were characterized by FT-IR, NMR, XRD, Raman and TEM analysis. Surface morphology and surface hydrophobicity behavior of the nanocomposites were also studied.

vi) Graphene oxide (GO) was prepared by using modified Hammer's method. Prepared GO was chemically reduced using $NaBH_4$ to obtain reduce GO (RGO). RGO was fictionalized using 2,4/2,6-toluene diisocyanate and monoglyceride of sunflower oil and the functionalized RGO was characterized using FT-IR, XRD, TGA, Raman and TEM analysis.

vii) IPN-based nanocomposites were fabricated using different weight% of functionalized RGO and characterized by using FT-IR, XRD, TGA, DSC and TEM analysis.

viii) Cu/RGO and Si/RGO nanohybrid was synthesized using hydrothermal technique and characterized using FT-IR, XRD, XPS, TGA and SEM analysis.

ix) Three different compositions were fabricated using different weight% of nanohybrid.

x) Fabricated nanocomposites were characterized by using FT-IR, XRD, TGA, DSC, FESEM and TEM analysis.

7. Salient Research Achievements:

Smart bio-based biodegradable high performing polymeric materials have been produced by conventional pre-polymerization technique. The silicone containing such polymeric materials exhibited self-healing, and self-cleaning along with shape memory effect. CNSL containing PU showed excellent self-healing behavior and anti-corrosive performance. Combined attributes of self-cleaning, shape memory and self-healing was achieved through IPN-based nanocomposites formation. Formation of mechanically tough self-cleaning IPN-based nanocomposites containing PS-g-MWCNT with excellent anti-icing property. IPN-based nanocomposites containing Cu/RGO showed excellent antimicrobial and antistatic property. IPN-based nanocomposites containing Si/RGO showed excellent anti-corrosion property.

7.1 Summary of Progress:

Bio-based HBPU was synthesized by using PCL, DAGP as a macroglycol, monoglyceride of sunflower oil as a chain extender, TDI as an aromatic diisocyanate and IPDI as an aliphatic diisocyanate. HBPUs with different amount of branching components were synthesized. The synthesized HBPUs were further characterized by using FT-IR, NMR and XRD.

Silicone containing HBPU with different compositions was synthesized by using PCL, PDMS, DAGP as a macroglycol, sunflower oil of monoglyceride as a chain extender, TDI as an aromatic diisocyanate and IPDI as an aliphatic diisocyanate. The synthesized HBPUs were further characterized by using FT-IR, NMR, XRD and SEM.

Silicone containing HBPU was further modified using calculated amount of CNSL as a chain terminating agent. Three different compositions were synthesized by simply varying the amount of CNSL. Synthesized PUs were characterized using different spectroscopic, microscopic and diffraction technique. Different properties (mechanical, thermal, self-healing and surface hydrophobicity) of the PUs were also evaluated.

A simultaneous interpenetrating polymer network (IPN) was prepared by using silicone containing PU and PS. Three different compositions were synthesized by changing the ratio of PU and PS. Synthesized IPNs were characterized by FT-IR, NMR, XRD and SEM.

Grafting of polystyrene into the defected sides of MWCNT was accomplished by using the radical polymerization technique and the grafting was supported by FT-IR, XRD, Raman, TGA and TEM analysis. Three different compositions were fabricated using the PS-g-MWCNT. Fabricated IPN-based nanocomposites were characterized by FT-IR, XRD, TGA, DSC, TEM and SEM analysis. After successful characterization, different properties like physical, mechanical, thermal, self-healing, self-cleaning and anti-icing are evaluated.

RGO was chemically functionalized using 2,4/2,6-toluene diisocyanate and monoglyceride of sunflower oil. Successful fictionalization of the RGO was supported by FT-IR, XRD, Raman, TGA and TEM analysis. Three different compositions were fabricated using different weight% of functionalized RGO and the fabricated IPN-based nanocomposites were characterized by FT-IR, XRD, TGA, DSC, TEM and SEM analyses. Then different properties of the fabricated nanocomposites were evaluated like mechanical, thermal, shape memory, self-cleaning etc.

Cu/RGO nanohybrid was prepared by using hydrothermal technique and characterized by FT-IR, XRD, XPS and TGA analysis. The change in surface morphology after nanohybrid formation was observed by SEM technique. After successful fabrication different properties like physical, mechanical, thermal, self-cleaning, anti static and anti microbial were evaluated.

Si/RGO nanohybrid was prepared hydrothermally and characterized by FT-IR, XRD, XPS and TEM analyses and the fabricated nanocomposites containing Si/RGO nanohybrid was characterized by FT-IR, XRD and TEM analysis. Surface morphology of the nanocomposites was characterized by using SEM analysis. Anti-corrosive behavior of the fabricated nanocomposites was analyzed electrochemically. In addition different properties like mechanical, thermal and self-cleaning properties were evaluated.

7.2 New Observations:

i) Synthesized HBPUs showed exceptional flexibility along with 100% self-healing efficiency.
ii) Silicone containing HBPUs showed exceptional flexibility along with self-healing, shape-memory and self-cleaning behaviour.
iii) Synthesized IPNs showed good flexibility along with self-healing, shape-memory and self-cleaning behaviour.

iv) Fabricated IPN-based nanocomposites containing PS-g-MWCNT showed excellent hydrophobic (static contact angle~143.6°) behaviour and anti-icing property (freezing delay time~2700s) with ultrafast self-healing ability.

v) Fabricated IPN-based nanocomposites containing PS-g-MWCNT showed moderate hydrophobic behaviour with ultrafast shape memory behaviour. Most-interestingly the nanocomposites also showed thermally actuated artificial muscle like behaviour.

vi) Fabricated IPN-based nanocomposites containing Cu/RGO nanohybrid showed outstanding elongation, moderate hydrophobic behaviour along with excellent antimicrobial property. Most-interestingly the nanocomposites showed good anti static behavior.

vii) Fabricated IPN-based nanocomposites containing Si/RGO nanohybrid showed excellent anticorrosion behavior.

7.3 Innovations:

(i) Silicone containing smart polymeric material with biodegradability.

(ii) PS-g-MWCNT containing IPN-based nanocomposites with excellent anti-icing behavior.

(iii) Cu/RGO containing IPN-based nanocomposites with excellent anti-microbial activity and anti static behavior.

(iv) Si/RGO containing IPN-based nanocomposites showed excellent anticorrosion behavior.

7.4 Application Potential:

7.4.1 Immediate : Bio-based biodegradable polymeric materials.

7.4.2 Long Term: As a mechanically tough self-healing, self-cleaning and anti-icing coating material.

7.4.3 Long Term: As a mechanically tough anti microbial surface coating with anti static attribute.

7.4.4 Long Term: As a mechanically tough, flexible, anticorrosive coating.

7.5 Any other: JRF has joined in the month of May 2017.

8. Research work which remains to be done under the project (for on-going projects)

As per the objective

- ✓ Hyperbranched polyurethanes with varieties of structures were synthesized by the conventional pre polymerization technique.
- ✓ Graphene oxide was prepared by modified hammers method and further reduced using conventional reducing agents (L-ascorbic acid, $NaBH_4$). Obtained RGO was further functionalized using monoglyceride of sunflower oil. In addition Cu/RGO and Si/RGO nanohybrid were synthesized separately using hydrothermal technique.
- ✓ Using these above prepared nanohybrids (Cu/RGO and Si/RGO) different nanocomposites were fabricated separately containing different dose of nanohybrid.
- ✓ Prepared nanohybrid and the fabricated nanocomposites were characterized using FTIR, XRD, Raman, XPS, SEM, FESEM and TEM analyses.
- ✓ Different properties like mechanical, thermal, self-healing, self-cleaning, anti-icing, shape memory, antistatic and antimicrobial properties of the nanocomposites were evaluated.
- ✓ Healing efficiencies of the fabricated nanocomposites were evaluated for some of the fabricated nanocomposites.
- ✓ A detailed structure property relationship was studied for each of the nanocomposites.

As per the objective there is no pending work

Ph.Ds Produced no: One is ongoing	Research Publications arising out of the present project: 5 (Five)

List of Publications emanated out of this Project (including title, author(s), journals & year(s)

(A) Papers published only in cited Journals (SCI)

[1] T. Ghosh, N. Karak, Biobased multifunctional macroglycol containing smart thermoplastic hyperbranched polyurethane elastomer with intrinsic self-Healing Attribute, ACS Sustain. Chem. Eng. 6 (2018) 4370–4381. doi:10.1021/acssuschemeng.8b00001.

[2] T. Ghosh, N. Karak, Silicone-containing biodegradable smart elastomeric thermoplastic hyperbranched polyurethane, ACS Omega. 3 (2018) 6849–6859. doi:10.1021/acsomega.8b00734.

[3] T. Ghosh, N. Karak, Tough interpenetrating polymer network of silicone containing polyurethane and polystyrene with self-healing, shape memory and self-cleaning attributes, RSC Adv. 8 (2018) 17044–17055. doi:10.1039/C8RA01766B.

[4] T. Ghosh, N. Karak, Multi-walled carbon nanotubes reinforced interpenetrating polymer network with ultrafast self-healing and anti-icing attributes, J. Colloid Interface Sci. 540 (2019) 247–257. doi:10.1016/j.jcis.2019.01.006.

[5] T. Ghosh, P. Bardhan, M. Mandal, N. Karak, Interpenetrating polymer network-based nanocomposites reinforced with octadecylamine capped Cu/reduced graphene oxide nanohybrid with hydrophobic, antimicrobial and antistatic attributes, Mater. Sci. Eng. C. 105 (2019) 110055. https://doi.org/10.1016/j.msec.2019.110055.

[6] T. Ghosh, N. Karak, Cashew nut shell liquid terminated self-healable polyurethane as an effective anticorrosive coating with biodegradable attribute, Prog. Org. coatings (2019, proof corrected)

[7] T. Ghosh, N. Karak, Sunflower oil modified hyperbranched polyurethane-polystyrene interpenetrating polymer network/functionalized-reduced graphene oxide nanocomposite as an advanced functional material, Compos. Part B Eng. (under review).

[8] T. Ghosh, N. Karak, Silica/reduced graphene oxide reinforced interpenetrating polymer network-based nanocomposites: As an advanced mechanically tough anticorrosive coating, Corros. Sci. (under review)

(B) Presentations in Conference/workshop/seminar, etc.

[1] T. Ghosh and N. Karak, Renewable resource based smart hyperbranched polyurethane elastomer (as poster presentation), International Symposium on Advanced Sustainable Polymers (ASP-17), IIT Guwahati, 8-11th January, 2018.

[2] T. Ghosh and N. Karak, Silicone containing bio-based hyperbranched polyurethane elastomer with smart attributes (as poster presentation), International Conference in Chemistry (Organix-2018), Department of Chemical Sciences, Tezpur University, 20th -21st December, 2018.

[3] T. Ghosh and N. Karak, Fabrication of interpenetrating polymer network-based nanocomposites of bio-based polyurethane and polystyrene with inherent surface hydrophobicity and shape memory attributes (as oral presentation), International Symposium on Sustainable Polymers & Launch of SPSI-North East Chapter, August 23-25th, 2019, IIT Guwahati, India.

Patents filed/ to be filed: Nil					
Major Equipment (Model and Make)					
S No	Sanctioned List	Procured (Yes/ No) Model & make	Cost (Rs in lakhs)	Working (Yes/ No)	Utilization Rate (%)
1.	Continuous flow stirred tank reactor (CSTR) with UV lamp and Flexible arm fume hood	Yes Fabricated	9,87,595/-	Yes	70%

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Annexure-II

ANNUAL INSTALMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE

1. SERB Sanction Order No and date : EMR/2016/001598 and 04 January 2017
2. Name of the PI : Professor Niranjan Karak
3. Total Project Cost : Rs. 2993518/-
4. Revised Project Cost (if applicable) : Not applicable
5. Date of Commencement : 25th January 2017
6. Statement of Expenditure : 01/04//2019 to 24/01/2020

(Month wise expenditure incurred during current financial year)

Month & year	Expenditure incurred /committed (Rs.)
April 2019	25000
May 2019	35000
June 2019	35000
July 2019	35000
August 2019	35000+24000
September 2019	35000
October 2019	35000+24050+27830
November 2019	35000+96122
December 2019	35000+89055+45382
Total expenditure up to 24th January, 2020	6,11,439/-

7. Grant received in each year:
   a. 1st Year: Rs. 16,59,025/-
   b. 2nd Year: Rs. 600000/-
   c. 3rd Year: Rs. 500000/-
   d. Interest, if any: Rs. 2754 (2nd year) + 4055 (3rd year)/-
   e. Total (a+b+c+d): Rs.27,65,834/-

Statement of Expenditure#

For the period of 01/04/2019 to 24/01/2020.

Sr. No.	Sanctioned Heads	Funds allocated(indicate sanctioned or revised)	Expenditure Incurred (in Rs.)				Total Expenditure (in Rs.)	Balance as on 24th January 2020 (in Rs.)	Requirement of Funds up to 24th January 2020 (in Rs.)	Remarks (if any) (in Rs.)
			1st year	2nd year	3rd year	Final year				
		(in Rs.)	25/01/2017 to 31/03/2017	01/04/2017 to 31/03/2018	01/04/2018 to 31/03/2019	01/04/2019 to 24/01/2020				
(I)	(II)	(III)		(IV)	(V)	(VI)	(VII)	(IX) = III – VII		
1.	Manpower costs	3,29,000/-	0	2,82,500/-	3,00,000/-	3,29,000/-	3,29,000/-	-	-	-
2.	Consumables	89055/-	0	1,53,443/-	1,47,988/-	89055/-	89055/-	-	-	-
3.	Travel	27945/-	0	26,896/-	30,099/-	27830/-	27830/-	115/-	-	-
4.	Contingency	46,492/-	0	42,131/-	49,940/-	45382/-	45382/-	1110/-	-	-
5.	Others (Interest)	4055	-	-	-	-	-	4055/-	-	-
6.	Equipment	24,180/-	0	9,67,600/-	0.0/-	24,050/-	24,050/-	130/-	-	-
7.	Overhead expenses	90712/-	0	73,179/-	80,619/-	96,122/-	96,122/-	-5410/-	-	-
8.	Total	6,11,439/-	0	15,45,749/-	6,08,646/-	6,11,439/-	6,11,439/-	Nil	-	-

Niranjan Karak

Name and Signature of Principal Investigator

Date: 18/02/20

Signature of Competent financial authority

(with seal) Finance Officer
Tezpur University

Date :

UC for Recurring Grant

UTILISATION CERTIFICATE
FOR THE FINANCIAL YEAR 2019– 2020 (UP TO 24th January)

UC pertinent to : **Third Release**

Is the UC Provisional : No

1. Title of the Project/ Scheme: **Investigation on structure-property relationship forself-healing smart hyperbranched polyurethane nanocomposite with antistatic and antimicrobial attributes**
2. Principal Investigator: PROFESSOR NIRANJAN KARAK
3. Implementing Institution: TEZPUR UNIVERSITY

4.	SERB Sanction Order No. and date :	**EMR/2016/001598** and 04th January 2017
5.	Amount brought forward from the previous financial year quoting SERB letter no and date in which the authority to carry forward the said amount was given	i. Amount:83,204/- ii. Letter/Order No.:EMR/2016/001598 iii. Date:15/07/2019
6a.	Amount received during the financial year (Please give SERB letter/order no and date)	i. Amount: Rs.5,00,000/- ii. Letter/Order No.: EMR/2016/001598 iii. Date:15/07/2019
6b.	Interest earned, if any	: Rs. 4055/-
7.	Total amount that was available for expenditure Rs. (excluding commitments) during the financial year (Sr. No. 5+6a +6b)	: Rs.5,87,259/-
8.	Actual expenditure incurred (excluding commitments during the financial year (upto24th January 2020)	: Rs. 5,87,389/-
9.	Balance amount available at the end of financial year (8-7)	: -130/-
10.	Unspent balance refunded to SERB, if any (please give details of cheque no etc.) Please allow to carry forward for the next financial year, 2019-2020	: Nil
11.	Amount to be carried forward to the next financial year (if any)	: Nil

UTILISATION CERTIFICATE

Certified that out of **Rs. . 5,87,259/-**of Recurring grants-in-aid sanctioned during the year **2019-2020** in favor of **Registrar, Tezpur University** under **SERB letter/ order No EMR/2016/001598 dated 04 January 2017** and a sum of **Rs. 5,87,389/-** has been utilized for the purpose of project for which it was sanctioned and the balance of **Rs.-130/-** remaining unutilized at the end of the year and is adjusted towards the Non-Recurring grants-in-aid.

Certified that we have satisfied ourselves that the conditions on which the grants-in-aid was sanctioned have been fulfilled/ are being fulfilled and that we have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned:-

Kinds of checks exercised.

1.
2.

Niranjan Karak

Signature of PI
the institute

Date 18/02/20

Signature of Registrar/Accounts officer

18/2/20

Finance Officer
Tezpur University

Date

Signature of Head of
Institute

Registrar
Tezpur University

Date

(To be filled in by DST)

Signature:_____
Designation:_____
Date:_____

UC for Non-Recurring Grant

UTILISATION CERTIFICATE
FOR THE FINANCIAL YEAR 2019– 2020 (UP TO 24th January)

UC pertinent to : **Third Release**

Is the UC Provisional : No

1. Title of the Project/ Scheme: **Investigation on structure-property relationship for self-healing smart hyperbranched polyurethane nanocomposite with antistatic and antimicrobial attributes**

2. Principal Investigator: PROFESSOR NIRANJAN KARAK

3. Implementing Institution: TEZPUR UNIVERSITY

4. SERB Sanction Order No. and date : **EMR/2016/001598** and 04 January 2017

5. Amount brought forward from the previous financial year quoting SERB letter no and date in which the authority to carry forward the said amount was given
   i. Amount: Rs.24,180/-
   ii. Letter/Order No.: EMR/2016/001598
   iii. Date: 15/07/2019

6a. Amount received during the financial year (Please give SERB letter/order no and date)
   i. Amount: Nil
   ii. Letter/Order No.: not applicable
   iii. Date: not applicable

6b. Interest earned, if any : Nil

7. Total amount that was available for expenditure Rs. (excluding commitments) during the financial year (Sr. No. 5+6a +6b) : Rs. 24,180/-

8. Actual expenditure incurred (including commitments) during the financial year (upto24th January 2020): Rs. 24,050/-

9. Balance amount available at the end of financial year (8-7) : Rs. 130/-

10. Unspent balance refunded to SERB, if any (please give details of cheque no etc.) Please allow to carry forward for the next financial year, 2019-2020 : Nil

11. Amount to be carried forward to the next financial year (if any) : Nil

UTILISATION CERTIFICATE

Certified that out of **Rs. 24,180/-** of Non-Recurring grants-in-aid sanctioned during the year **2019-2020** in favor of **Registrar, Tezpur University** under **SERB letter/ order No EMR/2016/001598 dated 04 January 2017** and a sum of **Rs. 24,050/-** has been utilized for the purpose of project for which it was sanctioned and the balance of **Rs. 130/-** remaining unutilized at the end of the year and is adjusted towards the Recurring grants-in-aid.

Certified that we have satisfied ourselves that the conditions on which the grants-in-aid was sanctioned have been fulfilled/ are being fulfilled and that we have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned:-

Kinds of checks exercised.
1.
2.

Niranjan Karak
Signature of PI
the institute

Date 18/02/20

Signature of Registrar/ Accounts officer

Finance Officer
Tezpur University

Date

Signature of Head of Institute

Registrar
Tezpur University

Date

Guidelines for preparation of UC

1. UC should be only for the grants released by the SERB. Please **do not account** for security deposits/other matching grants/account opening charges and miscellaneous items.
2. SERB Sanction No. and Dt should be accurately shown in the UC.
3. Even if the grant is unutilized in the financial year in which grant was released by SERB a NIL UC needs to be forwarded to SERB along with a request for carrying forward the grant to the next financial year. Such grants which are carried forward must be shown in the subsequent UC as carried forward grant and not amount received in the subsequent year (ref Sl. No. 5 on pre-page)

Science and Engineering Research Board

UC has been accepted by

Signature_____

Name of the SERB Officer_____

Designation_____