SELF-HEALING EPOXY POLYMERS: PREPARATION, CHARACTERIZATION AND APPLICATIONS

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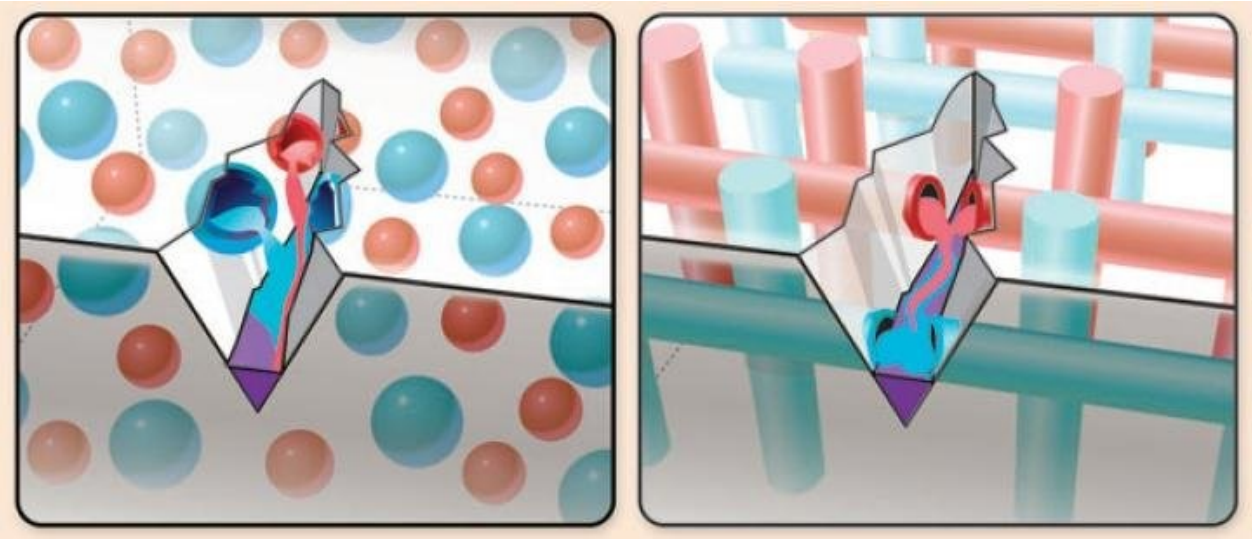
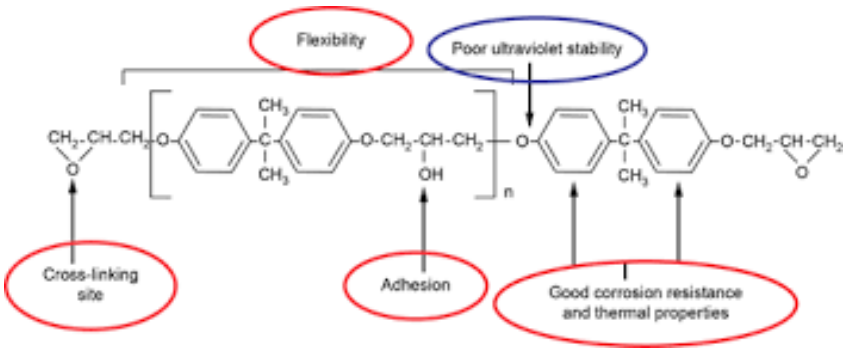


*" **Self-healing materials** are artificial or synthetically-created substances which have the built-in ability to automatically repair damage to themselves without any external diagnosis of the problem or human intervention"*

INTRODUCTION

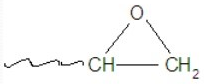
- Thermosets are generally supplied as a liquid
- Epoxy resin is second most widely used thermoset after Polyester.
- Epoxy also called "Epoxide" or "Polyepoxide"



- Most of epoxy used in non-reinforced (adhesives and paints etc.)
- Circuit boards are largest reinforced application (low conductivity and low volatile).

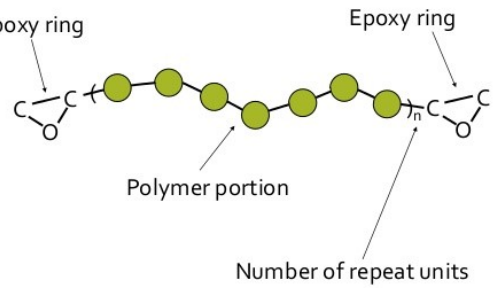
What are Epoxy resins?

- A family of thermosetting resins which have the following chemical group:



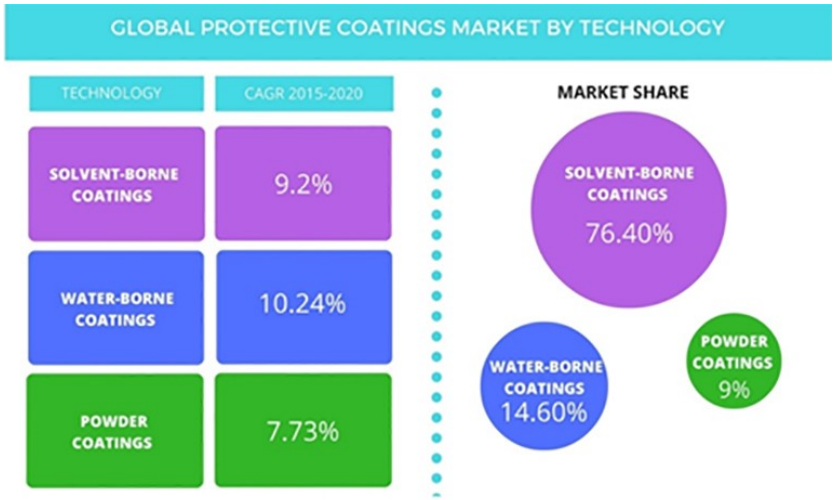
- When reacted with a hardener(or curing agent), they set to a hard mass which does not melt or dissolve in solvents.
- Hardeners are typically amine or anhydride based chemistry.

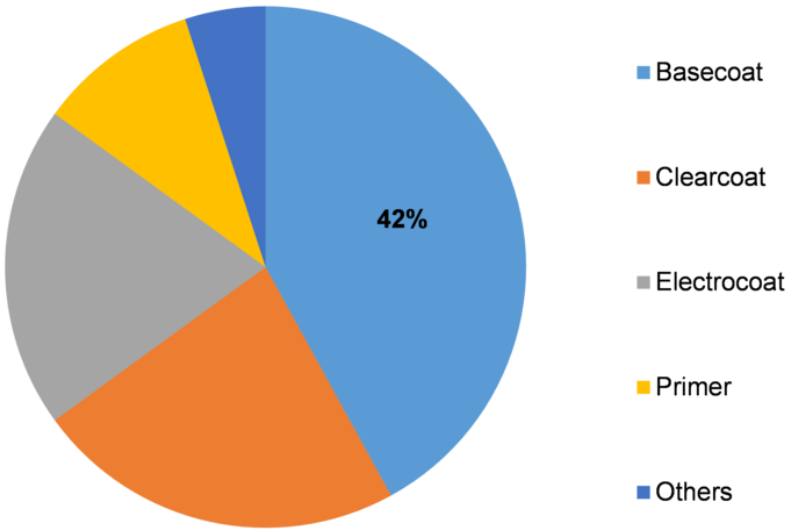
Epoxy Structure



APPLICATION SEGMENTS OF EPOXY RESIN IN EUROPE

COATING INDUSTRY TODAY
(WORLD MARKET)





- Paints and coating market
  - Global coatings market reached 8.7 billion gallons and USD107 billion in early 2019
  - Solvent and liquid coatings 75-80% of market.

BENEFITS OF EPOXY COATING

Some of benefits of epoxy coating experience, include:

- ❑ Safety
- ❑ Versatility
- ❑ Affordability
- ❑ Provide unique look
- ❑ Easy to clean and maintain
- ❑ Provide safety
- ❑ Durability
- ❑ Application time
- ❑ Longevity
- ❑ Convenience
- ❑ Variety of style
- ❑ The high performance of surface
- ❑ Improve surface integrity
- ❑ Control concrete dusting
- ❑ Protect concrete from wear
- ❑ Easy wash
- ❑ Protect substrate from degradation
- ❑ Flexible and efficient

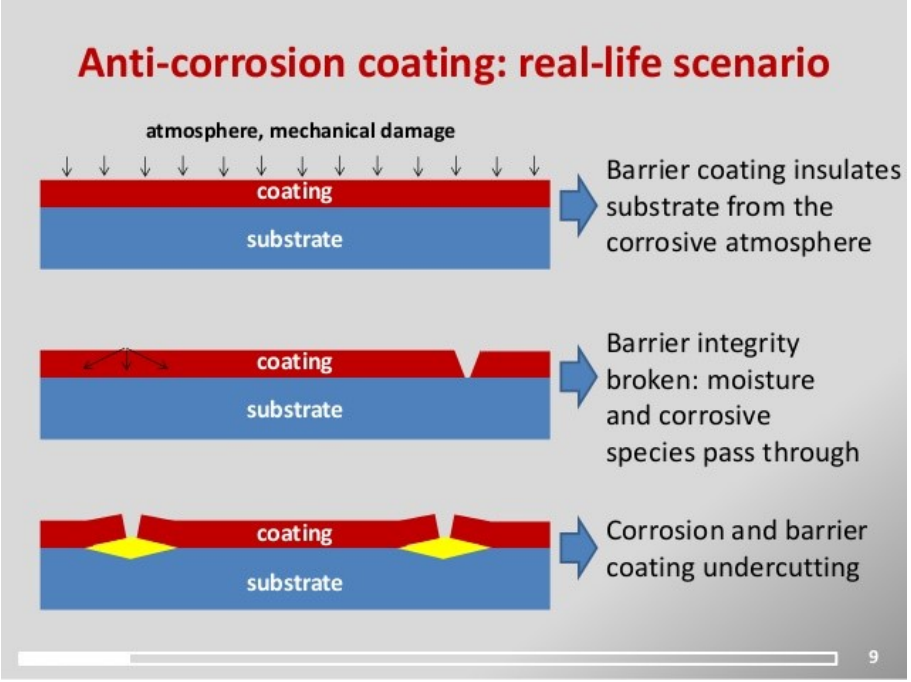
However UV stability is poor, corrosion prone due to microcracks

CORROSION IN METALS

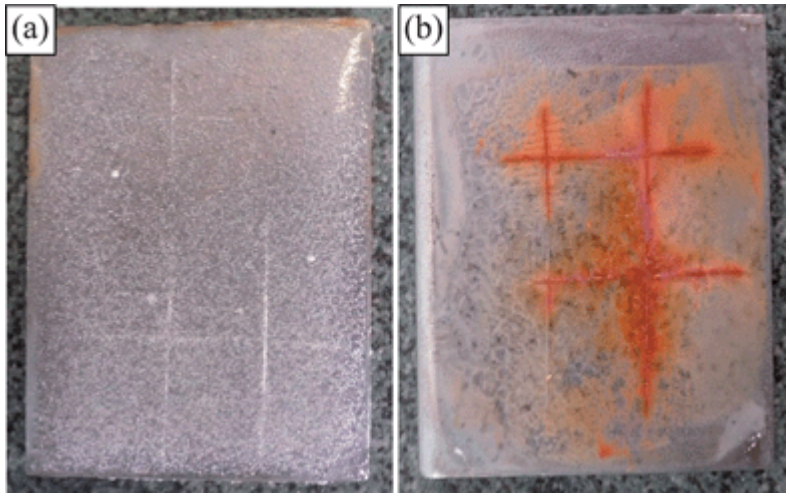
BACKGROUND OF STUDY

- A coating must protect its underlying substrate from harsh atmospheric conditions.

- Especially for metals that undergo corrosion.
- However, with time microcracks are developed within the coating.
- The cracks propagates faster and leads to failure in protection.
- Thus a smart protection that sense cracks and heal themselves.
- The solution: self-healing coating.



WHY SELF-HEALING ?



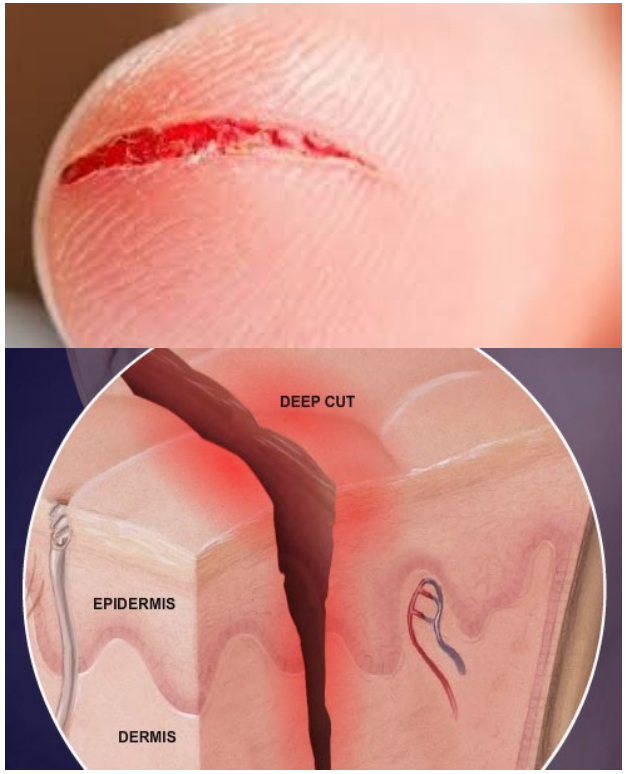
(a) Self-healing coating (b) Normal coating

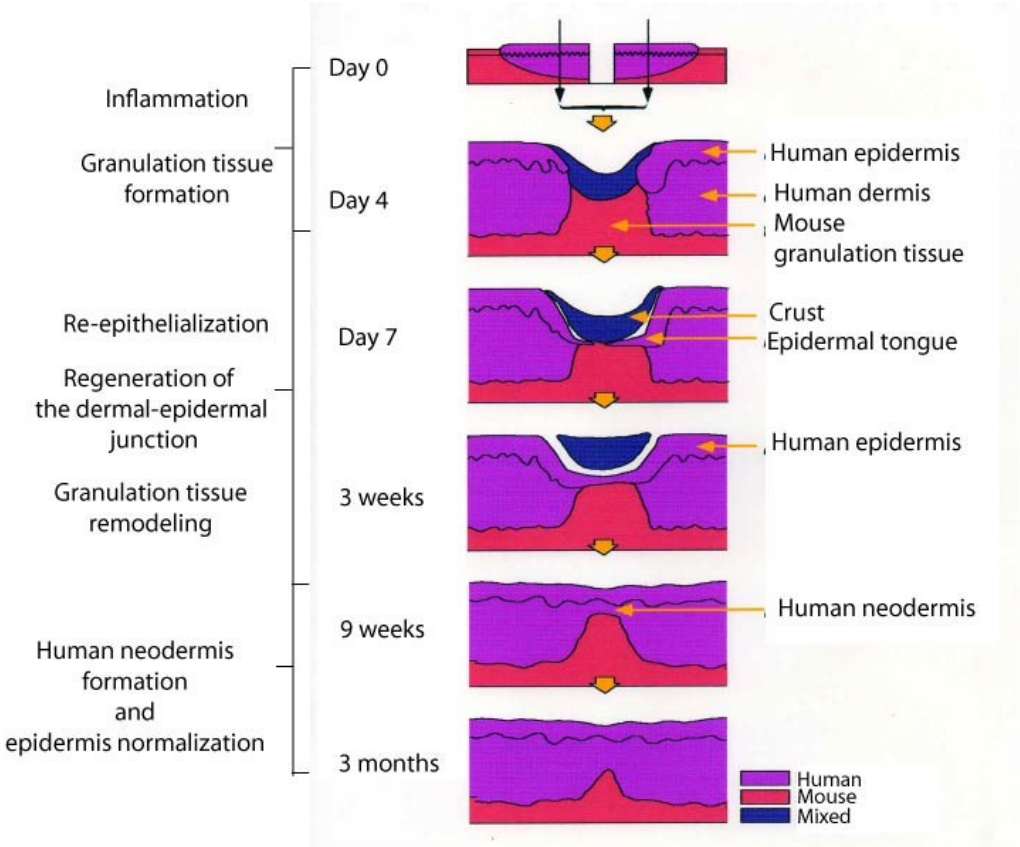
- ✓ Contribute greatly to the safety and durability of components.
- ✓ Capable of continuously sensing and responding to damage over the lifetime.
- ✓ Restoring the material performance.
- ✓ Offers great opportunities for broadening the applications.
- ✓ Recovery of properties such as fracture toughness, tensile strength.

Self-healing was inspired from nature by the process of "Biomimickry"

Self- healing polymeric materials : A review of recent developments, progress in polymer science, 2008.

HUMAN SKIN HEALING



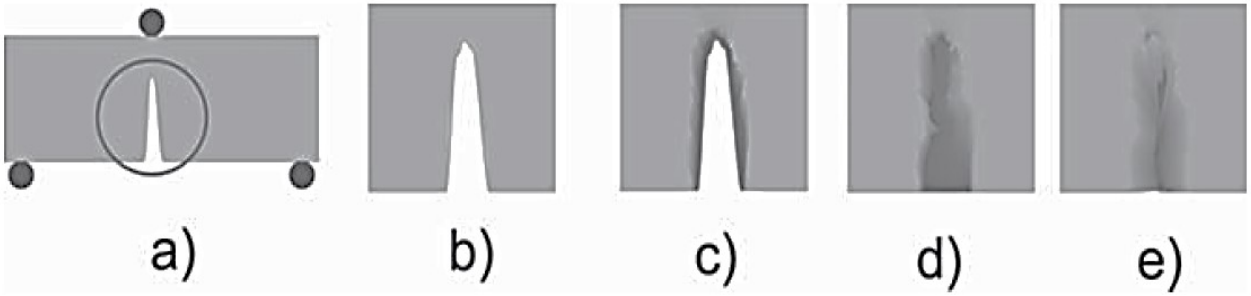


SELF-HEALING POLYMERS

- ✓ Self-healing materials are smart materials that can intrinsically repair damage leading to longer lifetimes, reduction of inefficiency caused by degradation and material failure.
- ✓ The inspiration comes from biological systems, which have the ability to heal after being wounded.
- ✓ Based on the nature of healing, they are mainly classified into autonomic and non-autonomic healing.

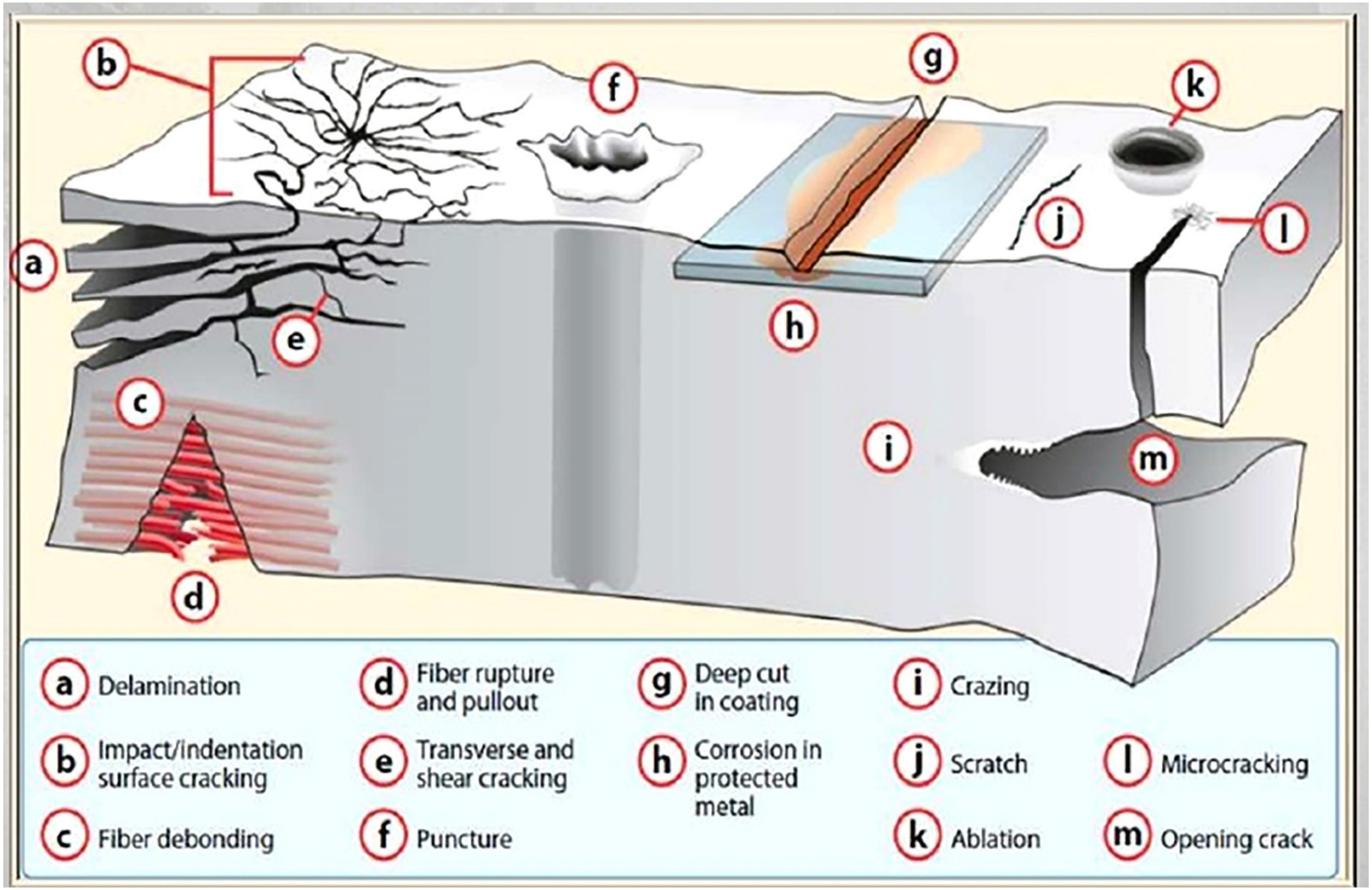
Autonomic	• Adaptive structures • Damage activates healing
Non-autonomic	• Need external stimulus like heat or light • Additional energy needed for healing

HOW SELF-HEALING WORK?

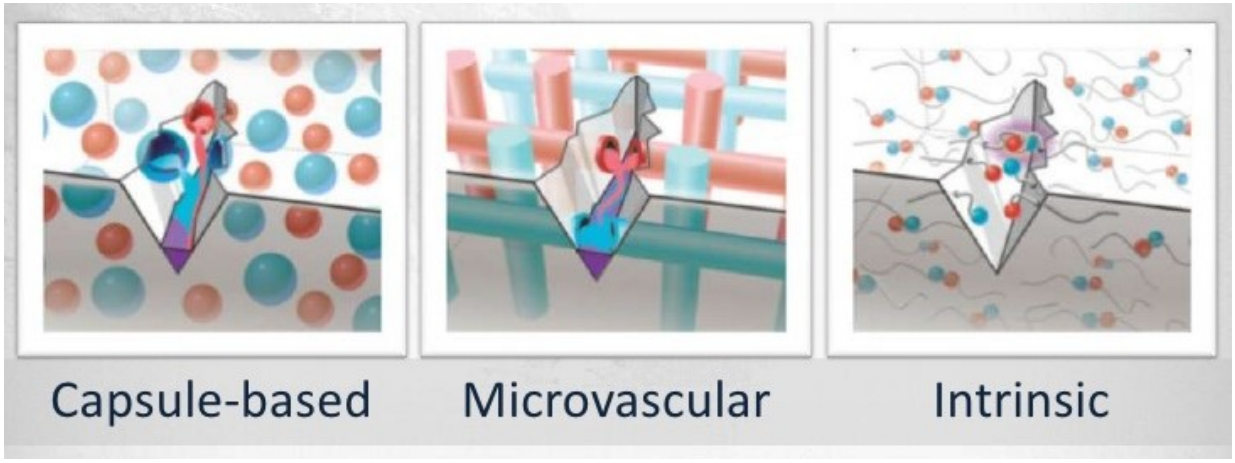


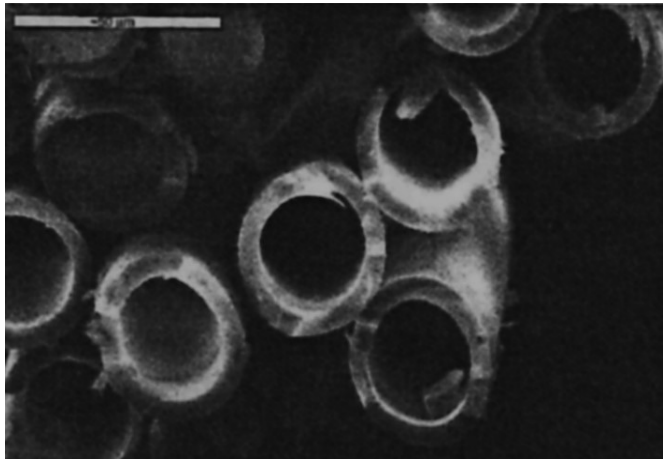
a) Damage is inflicted on the material
b) A crack occurs
c) Generation of "mobile phase" triggered by occurrence of damage or external stimuli
d) Closure of crack by "mobile phase"
e) Immobilization of mobile material after healing

DAMAGE OCCURRENCES



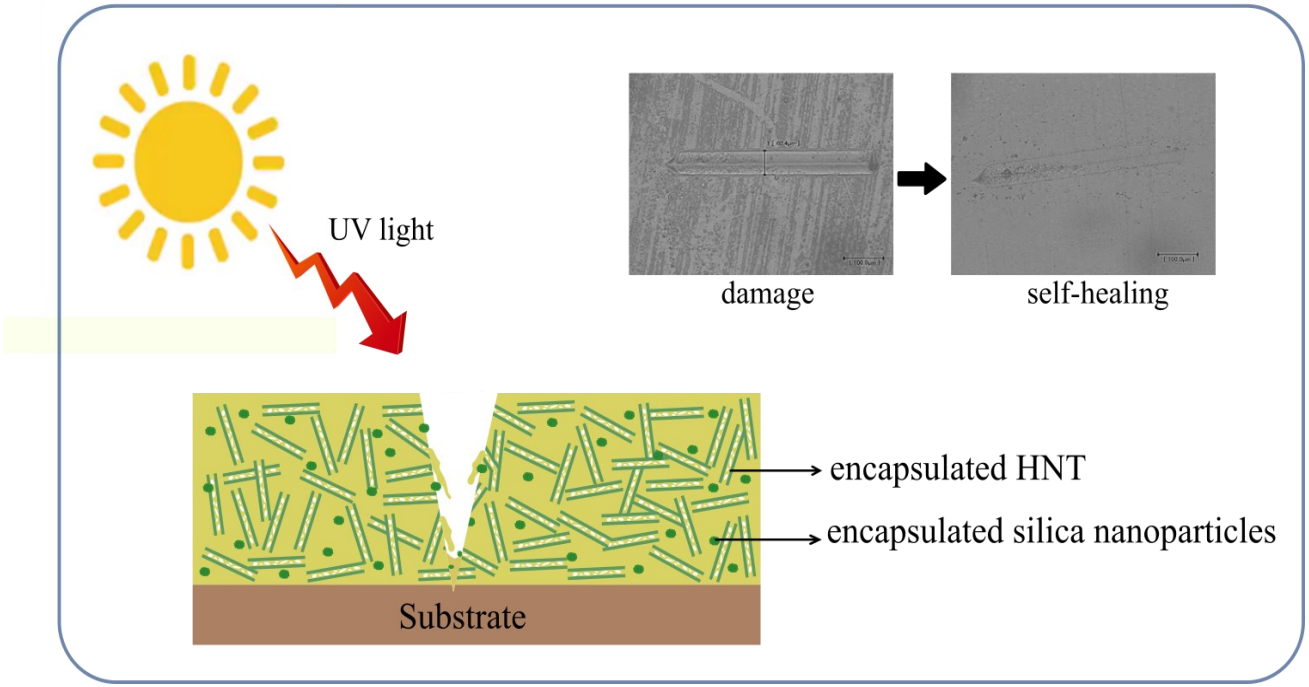
APPLICATIONS



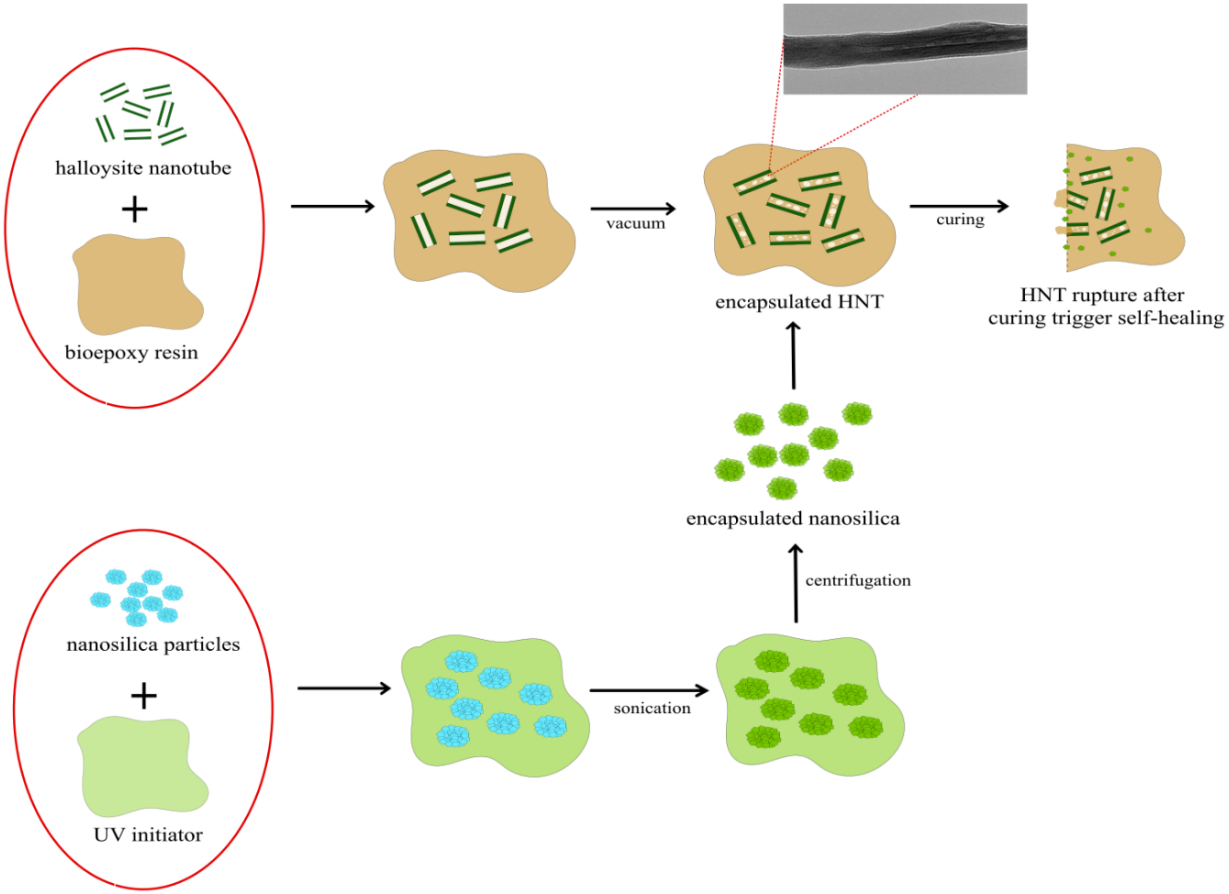


OBJECTIVE

- To develop self-healing coating that protect underlying metal substrates from corrosion.
- Use UV light (sunlight) for autonomous self-healing.



METHODOLOGY



Epoxy resin: SR Greenpoxy 56, Sicomin (Bio-based epoxy with 56% content from plants).
UV initiator: Triarylsulfonium hexafluorophosphate salts, Sigma Aldrich.
Hardener: SD surf clear, Sicomin.

TEM

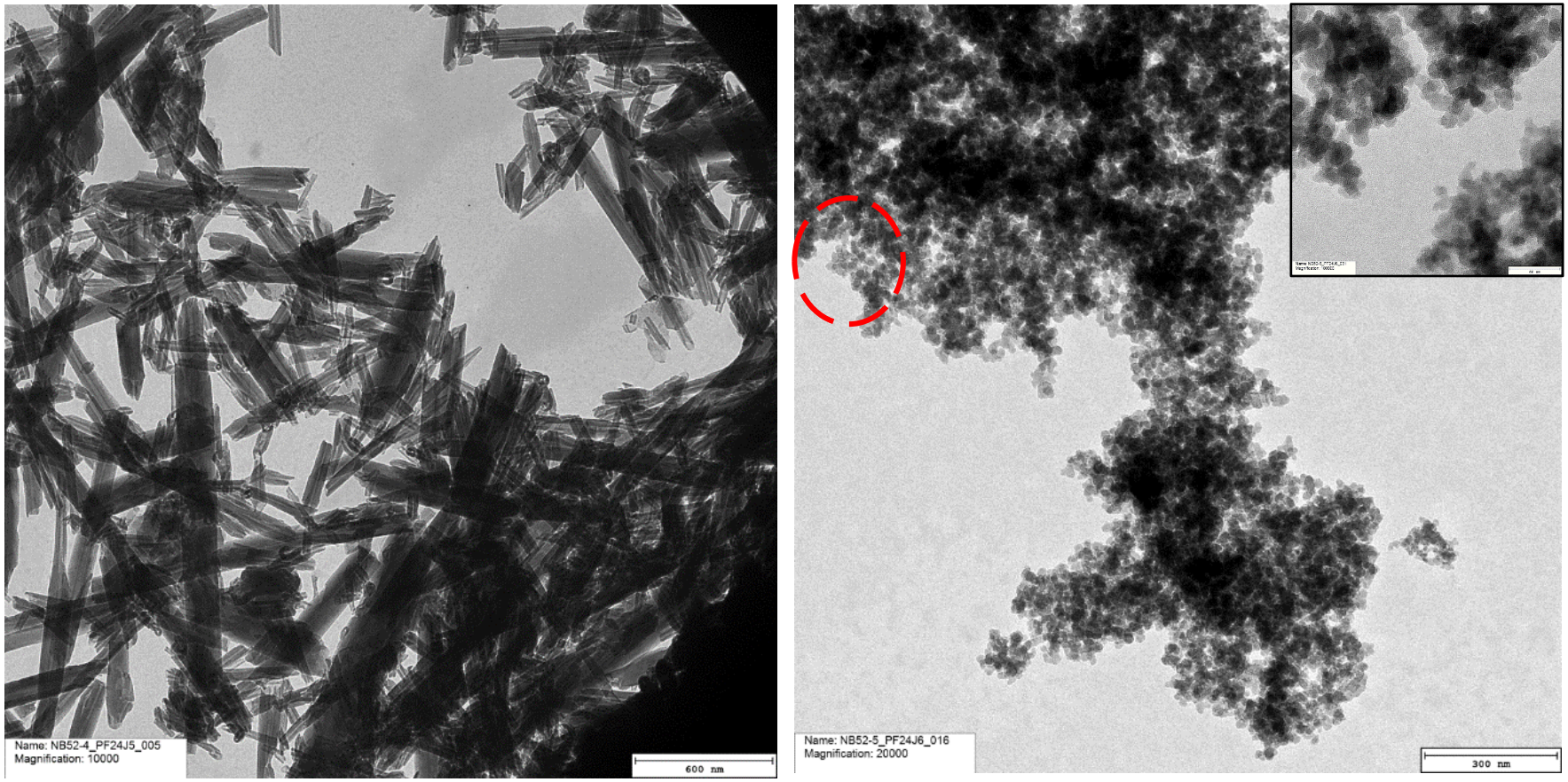
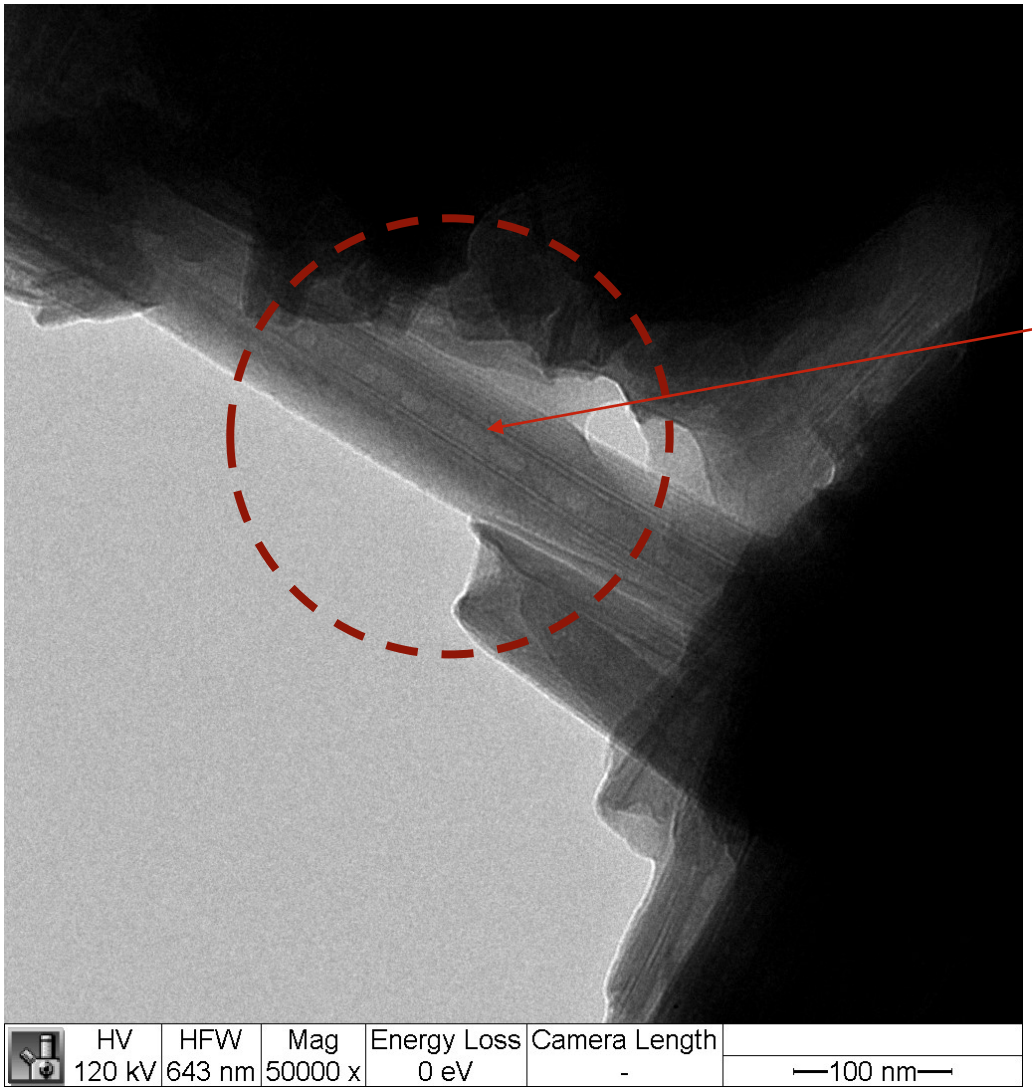


Fig. TEM image of (a) HNT (scale 600nm) and (b) nano-silica (scale 300nm, Inset scale 60nm.)

TEM (encapsulated HNT)



Air bubbles within encapsulated epoxy

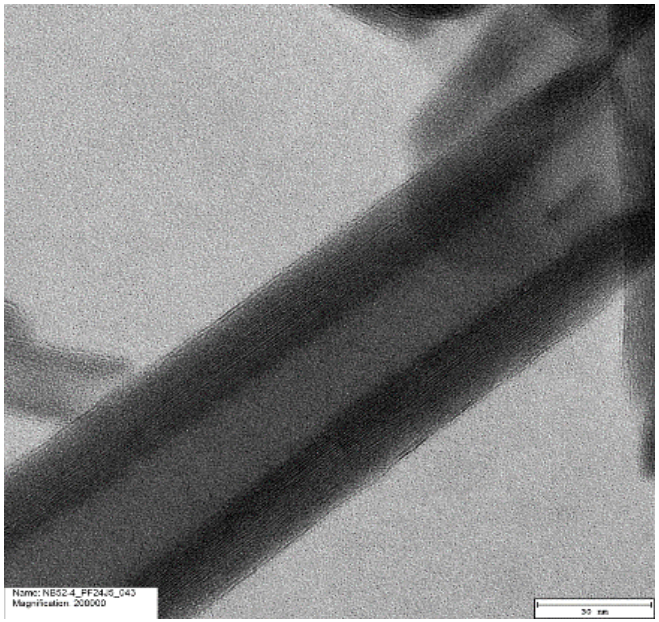


Fig. TEM image of filled HNT (scale 100nm)

Fig. TEM image of unfilled HNT (scale 30nm)

SAMPLES

Sample code	Epoxy (wt%)	Epoxy filled HNT (wt%)		UV initiator immobilized Silica (%)	
		Total amount of HNT+epoxy	Amount of epoxy encapsulated inside HNT	Total amount of silica+UV	Amount of UV initiator on silica
EP_{100}/HNT_0	100	0	0	0	0
EP_{95}/HNT_5	95	5	3.33	0.19	0.16
EP_{90}/HNT_{10}	90	10	6.67	0.40	0.33
EP_{80}/HNT_{20}	80	20	13.33	0.80	0.67
EP_{70}/HNT_{30}	70	30	20.00	1.20	1.00
EP_{60}/HNT_{40}	60	40	26.67	1.60	1.33

The HNT and epoxy is mixed in 1:2 ratio. The silica and UV initiator mixed in 1:5 ratio.

FTIR SPECTRA

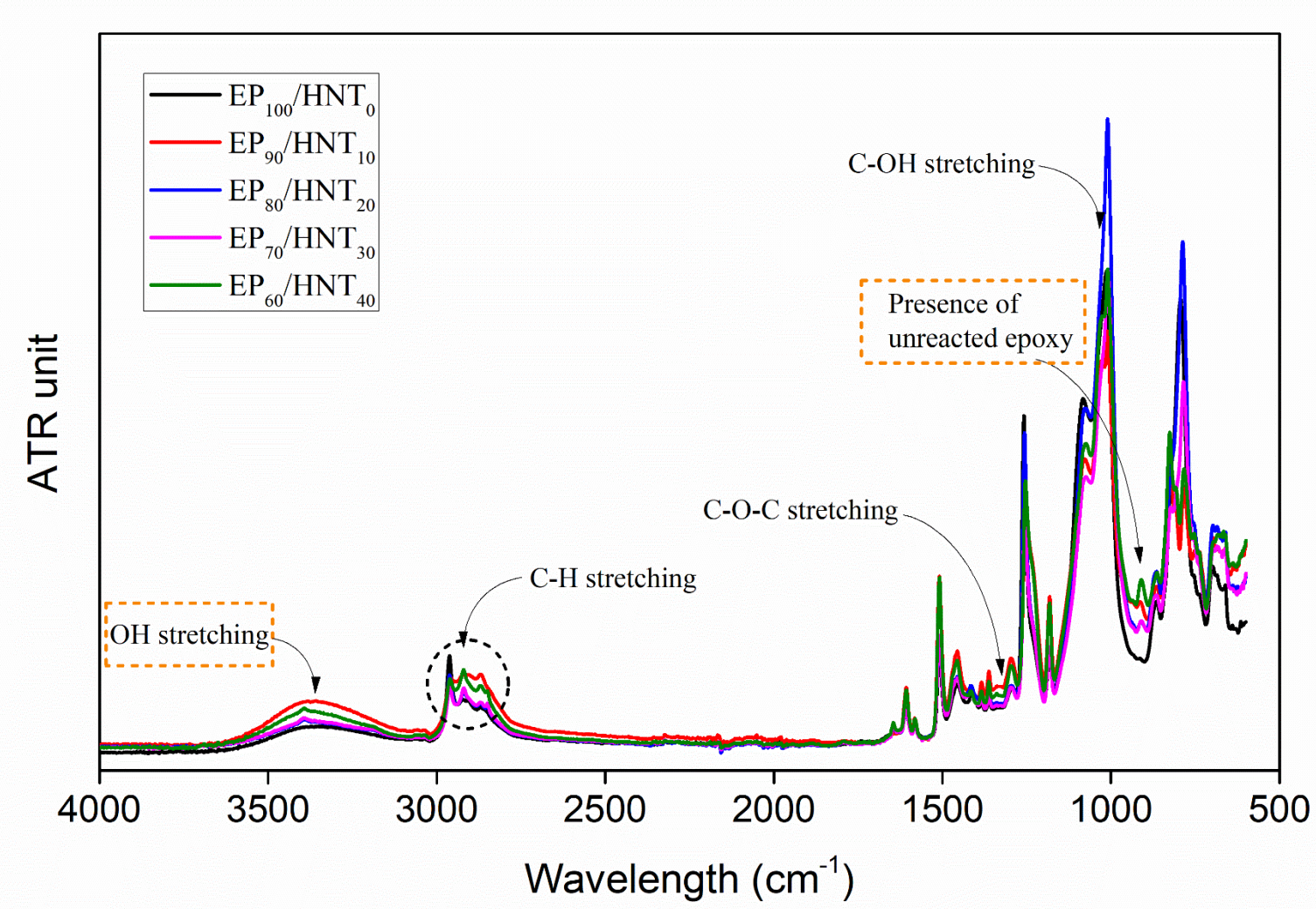


Fig. The FTIR spectrum of Epoxy composites with different weight percentage of encapsulated HNT and silica.

MECHANICAL PROPERTY

Sample code	Tensile strength (MPa)	Elongation at break (%)	Youngs Modulus (MPa)
EP_{100}/HNT_0	53.7 ± 4.6	11.7 ± 0.5	810.9 ± 91.2
EP_{95}/HNT_5	46.9 ± 7.8	9.8 ± 1.5	845.0 ± 61.6
EP_{90}/ HNT_{10}	50.9 ± 3.8	8.6 ± 1.2	964.1 ± 63.5
EP_{80}/HNT_{20}	44.2 ± 3.1	7.2 ± 0.8	1018.9 ± 75.5
EP_{70}/HNT_{30}	37.8 ± 3.4	6.2 ± 0.7	981.8 ± 54.3
EP_{60}/HNT_{40}	31.7 ± 0.6	14.8 ± 2.6	682.8 ± 35.2

SEM ANALYSIS

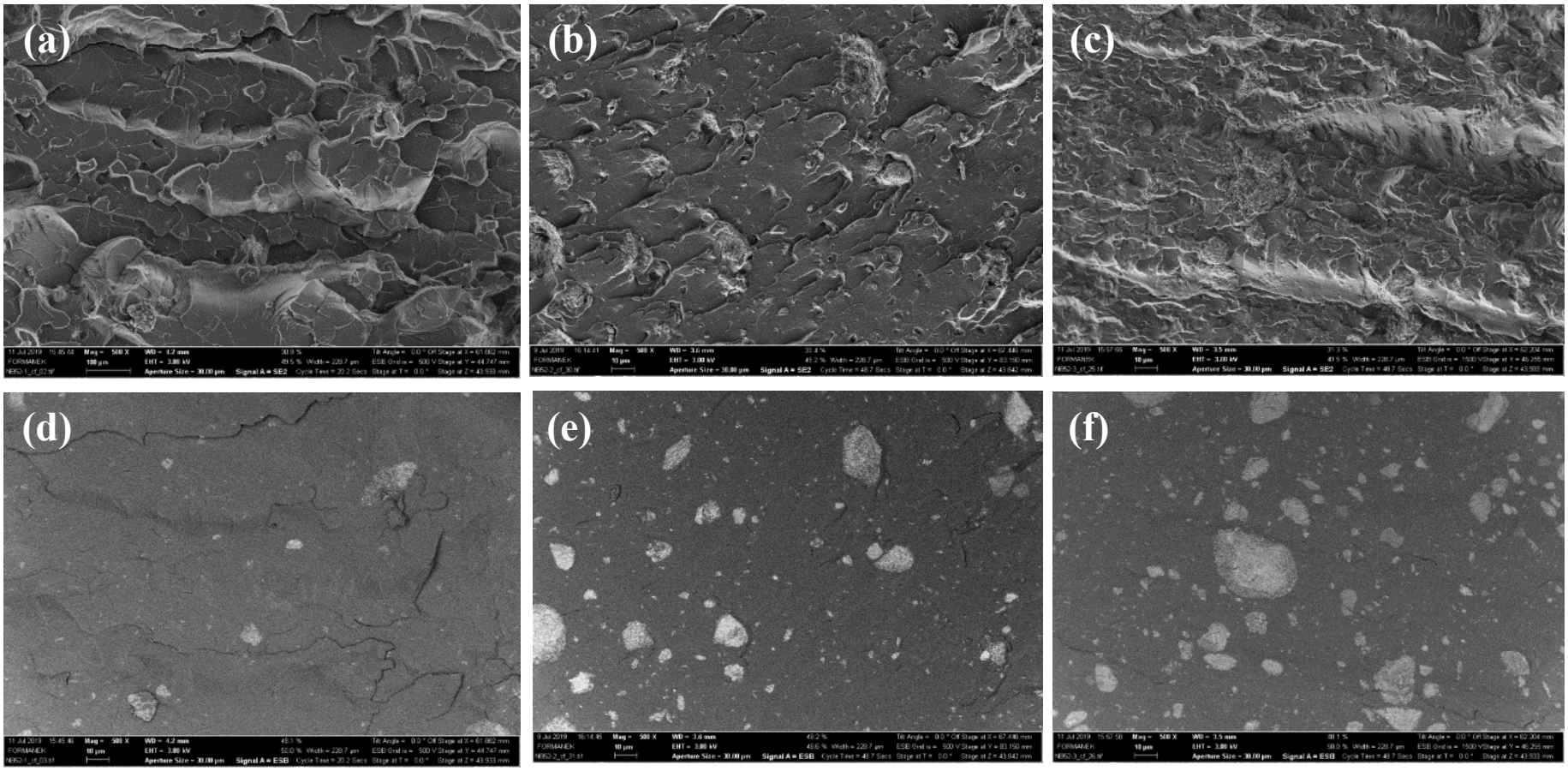
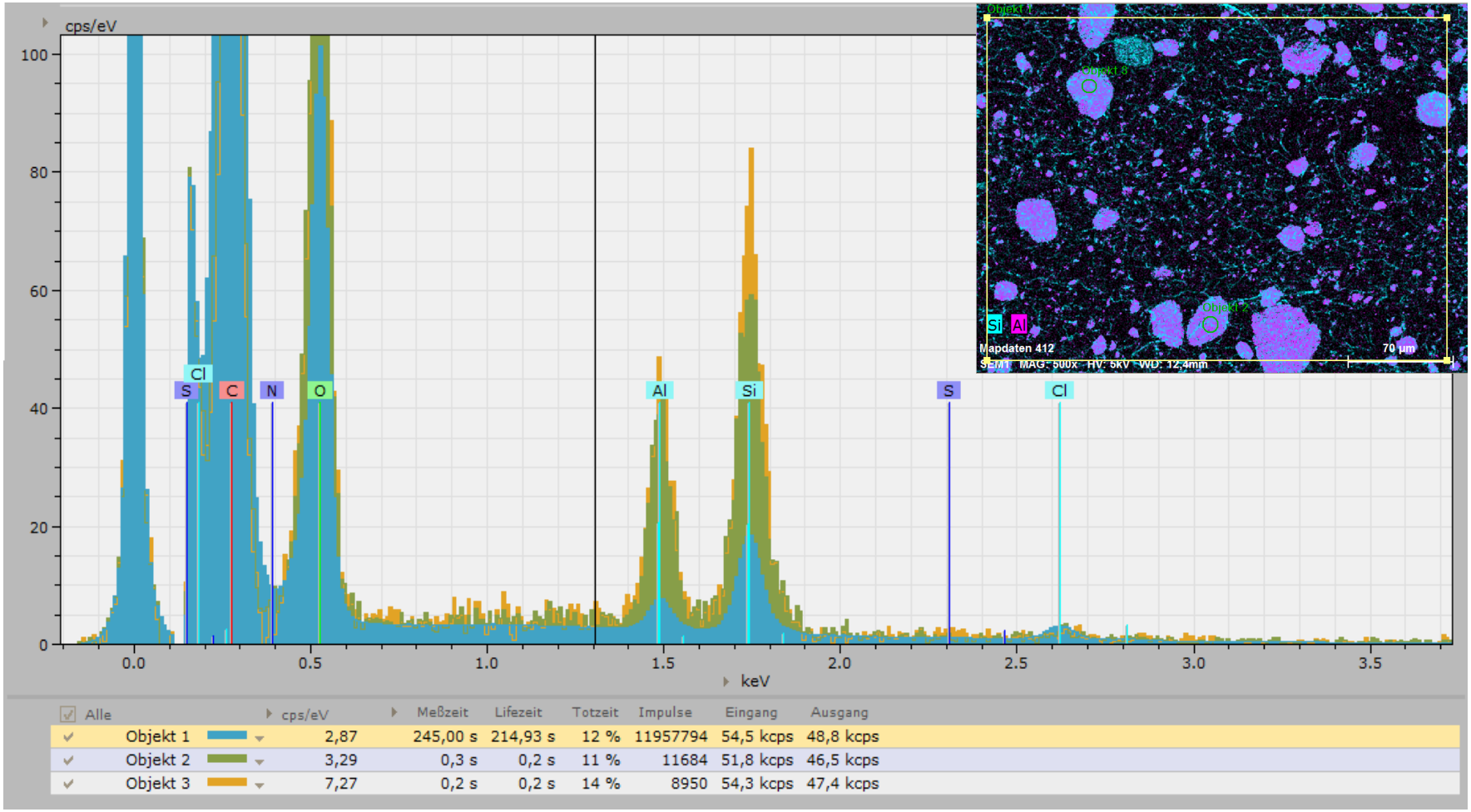


Fig. SEM images with (a), (b) and (c) is topography using secondary electron of 5wt%, 20wt% and 40wt% HNT and (d) (e) (f) their corresponding SEM images with back scattering electrons showing the dispersion of HNT and silica clearly

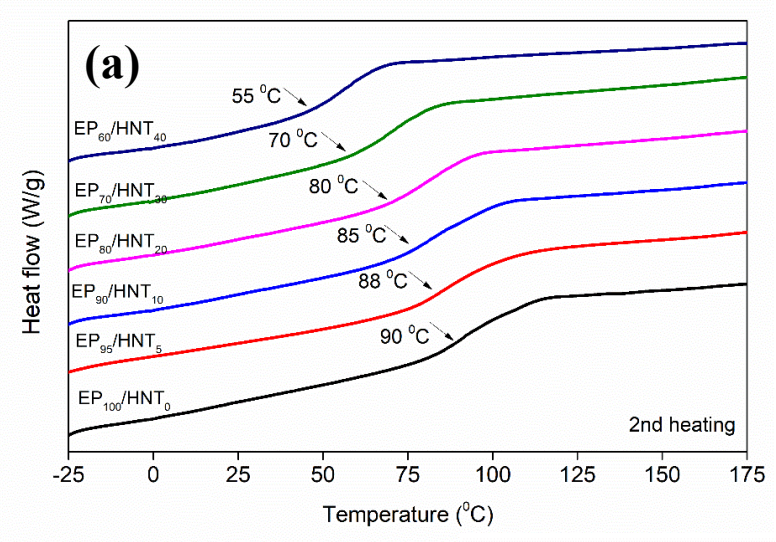
EDX

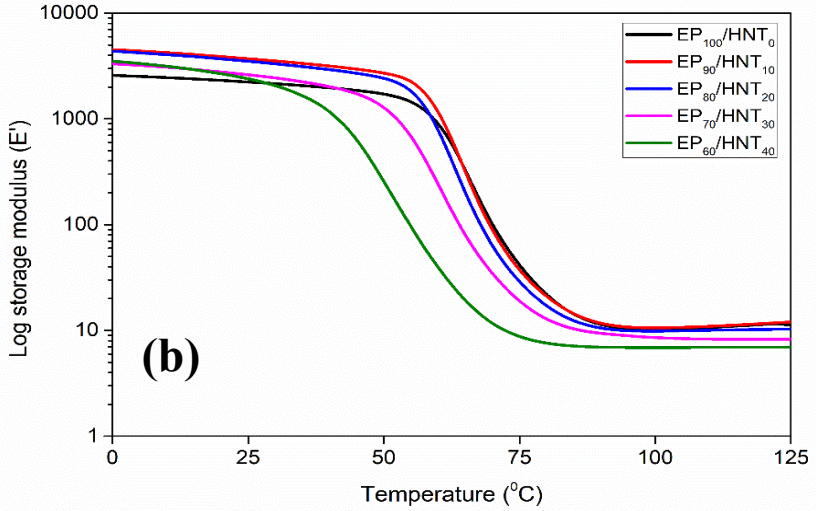


Alle	cps/eV	Meßzeit	Lifezeit	Totzeit	Impulse	Eingang	Ausgang
Objekt 1	2,87	245,00 s	214,93 s	12 %	11957794	54,5 kcps	48,8 kcps
Objekt 2	3,29	0,3 s	0,2 s	11 %	11684	51,8 kcps	46,5 kcps
Objekt 3	7,27	0,2 s	0,2 s	14 %	8950	54,3 kcps	47,4 kcps

Fig. Energy dispersive X-ray spectroscopy of 40wt% HNT

THERMAL ANALYSIS





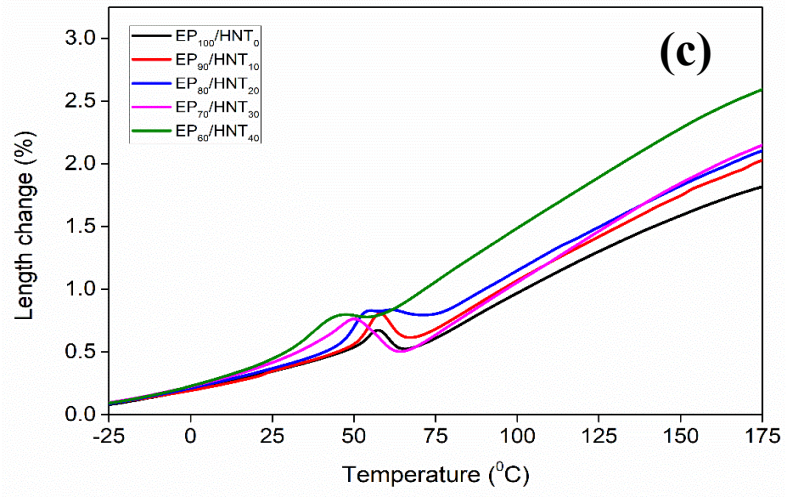


Fig. (a) DSC thermogram, (b) Storage modulus with DMA and (c) TMA

THERMAL DEGRADATION

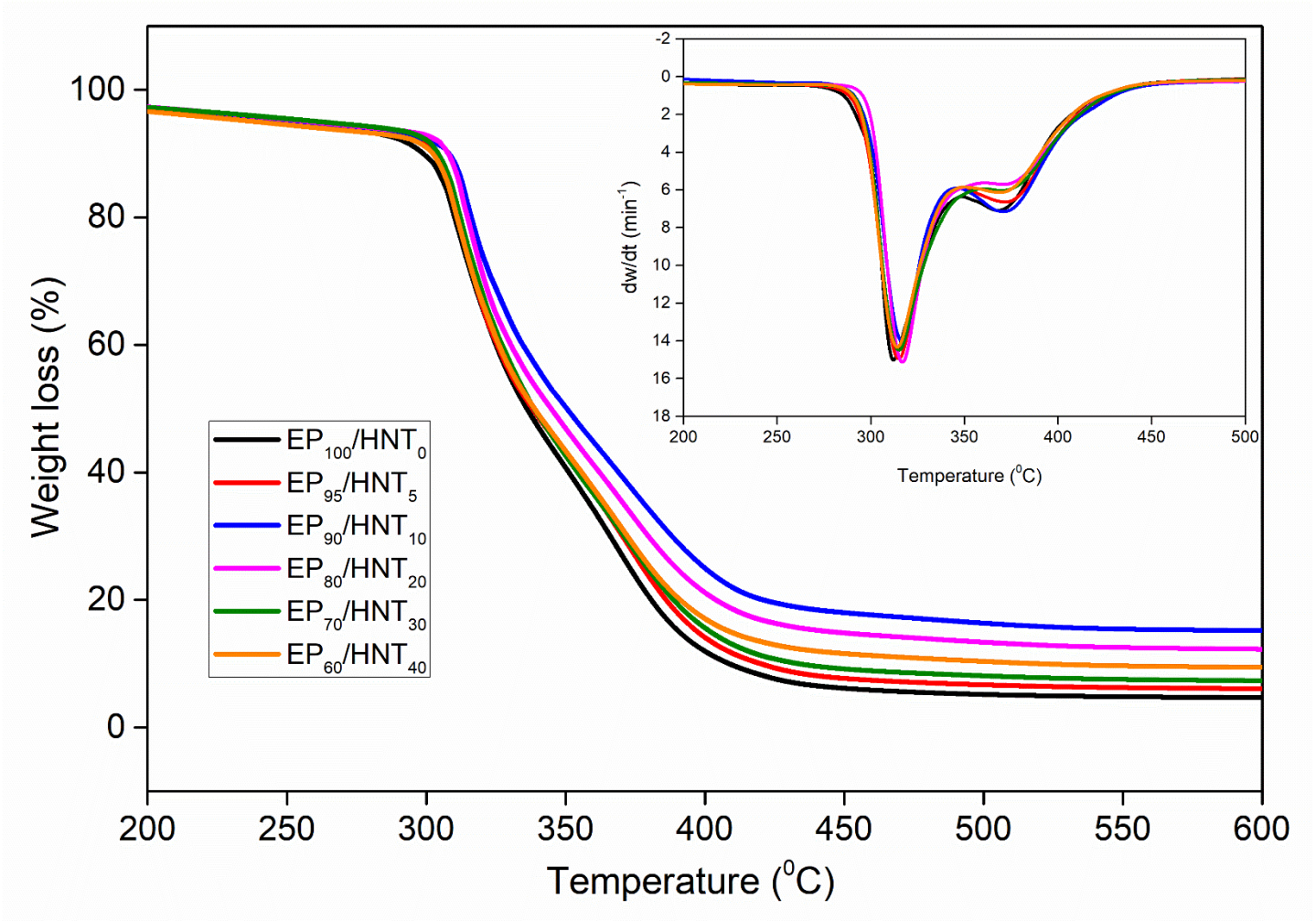


Fig. TGA graph (inset: DTG)

NANO-INDENTATION SCRATCH TEST

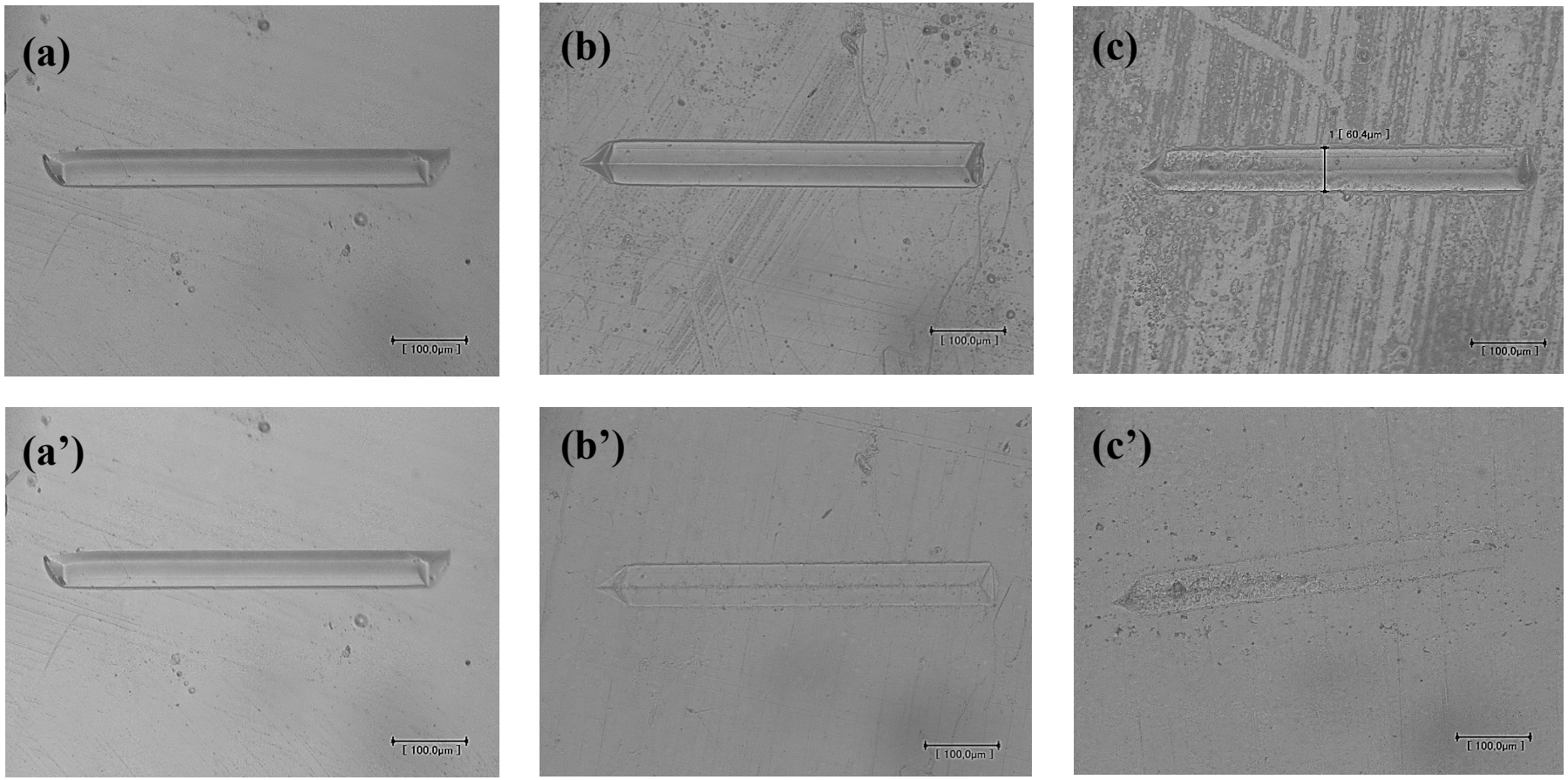


Fig. (a) (b) and (c) represents scratch made with a constant force of 200mN on EP_{100}/HNT_0, EP_{80}/HNT_{20} EP_{60}/HNT_{40} respectively; (a') (b') and (c') is corresponding specimen after 15min in sunlight.

CONCLUSION

- The prepared self-healing coating were investigated with nano-indentation scratch test.
- Successful healing was observed on the scratch surface at 40 wt% HNT loading.
- TEM analysis and FTIR spectroscopy shows the presence of encapsulated epoxy.
- SEM and EDX shows the distribution of HNT and silica nanoparticles.
- DSC studies and DMA show reduction in Tg with increase in HNT content due to plasticizing effect of HNT and silica nanoparticles.
- TGA studies show marginal improvement in degradation temperatures.

ACKNOWLEDGEMENT

- My mentors Prof. Dr. –Ing habil Suchart Siengchin and Prof. Dr. Jyotishkumar Parameswaranpillai
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THANK YOU !!

Please feel free to ask any queries….

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"Your preparation for the real world is not in the answers you've learned, but in the questions you've learned how to ask yourself"