Auto Curing of Composites with Strength Recovery using Nanotechnology

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Abstract— This presentation is about the problems involved in the curing of the spacecraft structures made of composite materials, onboard without any human intervention. This is possible only by applying the concept of auto curing to the composites. We mainly eye on gaining back the strength of composite structures which is auto cured so as to withstand further impact loads. This can be achieved by using functionalized carbon nano tubes (CNT) thus solving the problem of crack propagation in spacecraft and aircraft applications like electrical wiring, pipes and other applications like bridges, circuit boards, tennis ball etc. thereby strengthening the structure, increasing its life time, reducing the repairing costs and ensuring utmost safety.

Key words: Epoxy Polymer Composites, CNT, Microencapsulated Curing Agent, Grubb's Catalyst, Dicyclopentadiene, Acetyl Acetonovate

Technical Field: This presentation relates generally to composite material structures and more specifically in applying the concept of nanotechnology to the same in an effective manner.

I. Introduction

Composites used for spacecraft typically have a polymer matrix made from thermosetting (epoxies, phenolics, and polyimides) resins reinforced with aramid, carbon, or glass fibers. But there is a common weakness with most composite structures: They don't tolerate impacts, i.e., they have low fracture toughness and don't resist crack propagation. Impact loads typically generate micro cracks in the "through thickness" direction where damage tolerance in composites is at its lowest. The auto cure composite system helps sealing the cracks by itself. This technology could be the first step in building a spacecraft capable of traveling millions of miles from Earth, where repairs won't be easy to make. However this system does not give the composite its original strength. How to regain it back???

II. About Fibre Reinforced Composites

Fibre Composites consist of polymers (plastics) reinforced with carbon, glass and/or aramid (Kevlar) fibres. These materials are up to 6 times stronger than steel and concrete at a fraction of the weight. They are also non-corroding, non-magnetic and can be designed to locate strength and stiffness where it is needed.

A. Specific advantages of fibre composites in structural engineering include

1) More appropriate and economical structures:

Case histories demonstrate that in many applications (even with today's material costs and processing technologies) fibre composites are directly competitive in initial cost, substantially less expensive in terms of installed cost, and far less costly in maintenance.

2) More attractive structures:

Because of the high strength, low weight and excellent design flexibility, fibre composite structures are commonly smaller, easier to blend in with the environment and more pleasing to the eye.

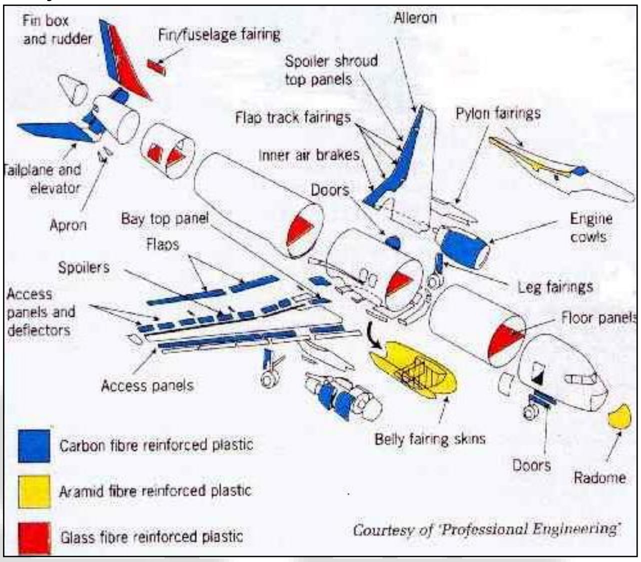


Fig. : Composites in different parts of an aircraft

3) More environmental friendly structures:

The high corrosion resistance of fibre composites eliminates the need for chemical treatment (as required for most timbers), or protection by toxic paints (as with steel). Consequently there is less danger of leaching of dangerous chemicals into the environment.

4) Composite materials are also becoming more sustainable:

Significant effort is being made in the development of polymer resins made from plant oils. Soy based resins are already in use for non-structural components, and natural fibres such as flax are being used to create sustainable composites from renewable resources.

Despite these many advantages, the major drawback in using composites in spacecrafts is that its tendency to crack with time. Especially, due to extreme heat and pressure encountered in space, the composite material cracks easily. That is why there is a must for crack prevention technique in these composites.

B. How Cracks are Formed

The heating of a spacecraft during the reentry phase, leads to the oxidation of the surface causing a loss of catalycity properties of the material. The heating due to the transfer of the kinetic energy from the plasma is created in the nozzle of the spacecraft. Oxygen atoms created from this plasma recombine on the surface leading to an additional increase of the temperature from 373 K to 773 K depending on the catalycity of the thermal protection material and its partial degradation. The diffusion of oxygen in the bulk increases the porosity which causes damage to the surface. The damage may involve bond rupture, the formation of micro voids, debonding of the fibres from the resin, or various other events at the molecular and microscopic levels that collectively weaken the material and perhaps put its user at risk. The most common route to failure is fatigue — the formation of micro voids incurred by mechanical stress through repeated usage. The micro voids enlarge and coalesce to form micro cracks in the material. These cracks are invisible to the eye and can also form underneath the surface of the material, where they are hidden from sight. Once these cracks form, they will grow until the material weakens and breaks.

C. What is Auto Curing?

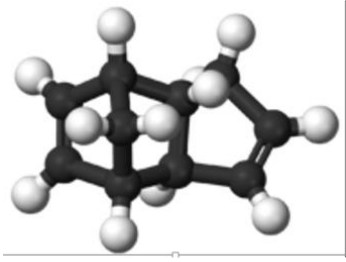
If we cut ourselves with a knife the wound formed will slowly start healing by the formation of new skin. This is the best example of self-healing found within us. In order to prevent the tiny cracks formed in spacecrafts from spreading, a new material has been developed that will sense damage and mend itself instantly. This self-healing ability could significantly prolong the life of the spacecraft.
There are three parts to this new self-healing material:

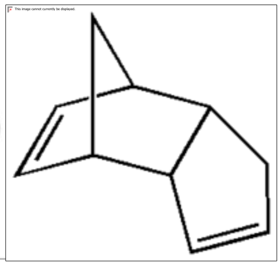
1) Composite material:

The bulk of the material is an epoxy polymer composite. Polymer composites are advanced materials that are made from carbon, glass or Kevlar and a resin, such as epoxy, vinyl ester or urethane.

2) Microencapsulated curing agent:

This is the glue that fixes the micro cracks formed in the composite material. This healing agent is a fluid called Dicyclopentadiene; DCPD (a white crystalline solid with a camphor-like odor).This fluid is encapsulated tiny bubbles that are spread throughout the composite material. There are about 100- 200 capsules per cubic inch. Along with DCPD, we enclose carbon nano tubes to increase the strength of the new composite.





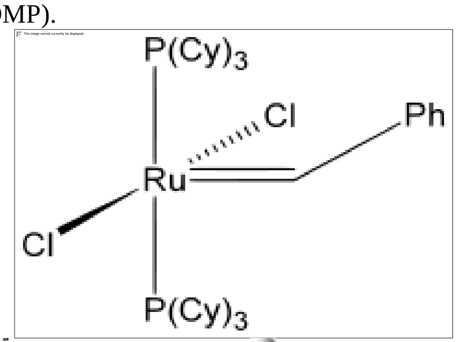
D. Dicyclopentadiene

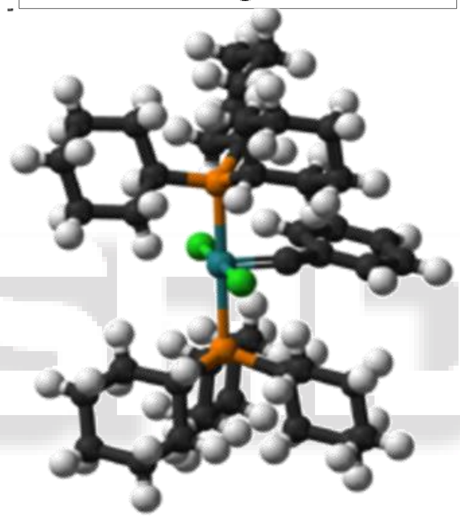
IUPAC name□ tricyclo[5.2.1.0^{2,6}]deca-3,8-diene, Other name□ 1,3-Dicyclopentadiene

1) Properties of Dicyclopentadiene:

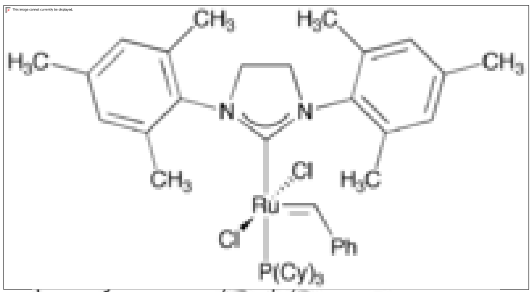
Molecular formula□$C_{10}H_{12}$, Molar mass □132.20 g/mol, Density□ 0.98 g/cm^3 -□,Melting point□ 32.5 °C
Boiling point 170 °C, Flash point 32 °C. It is used in resins, inks, adhesives and paints.

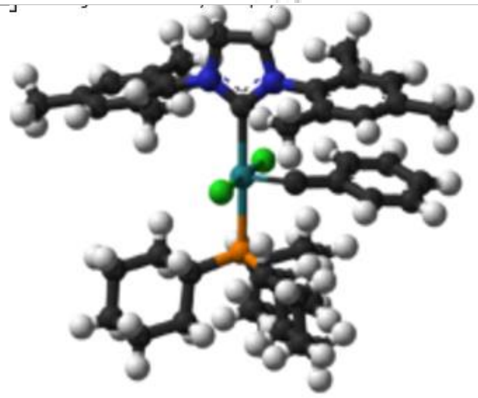
- Catalyst - In order to polymerize, the healing agent must come into contact with a catalyst. A patented catalyst, called Grubbs' catalyst, is used for this self-healing material. It is important that the catalyst and healing agent remain separated until they are needed to seal a crack.
- Grubbs' Catalyst 1st Generation
- IUPAC name□ bis (tricyclohexylphosphine) dichlororuthenium, General Molecular formula□ $C_{43}H_{72}Cl_2P_2Ru$ Molar mass□ 822.96 g/mol, Appearance□ Purple Solid, Melting point□ 153 °C (426 K) it is used in organic synthesis to achieve olefin cross-metathesis, ring-opening metathesis polymerization (ROMP).





E. Grubbs' Catalyst 2nd Generation

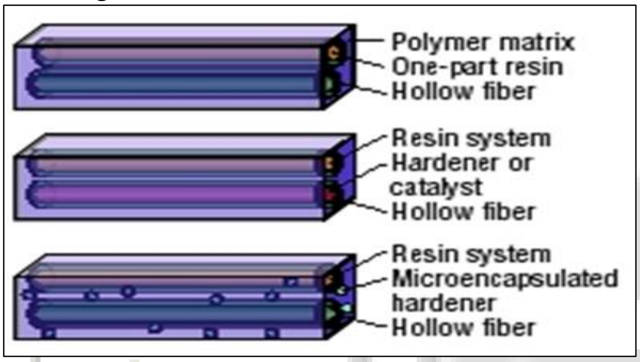




IUPAC name□ benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (tricyclohexylphosphine)ruthenium, General Molecular formula□ C46H65Cl2N2PRu, Molar mass□ 848.97 g/mol, Appearance□ Pinkish-Brown Solid, Melting point□143.5-148.5 °C (416.5-421.5 K). It has the same uses in organic synthesis as the First Generation Catalyst, but has a higher activity. This catalyst is oxygen and water sensitive and so should be handled under a nitrogen or argon atmosphere.

F. How it Works?

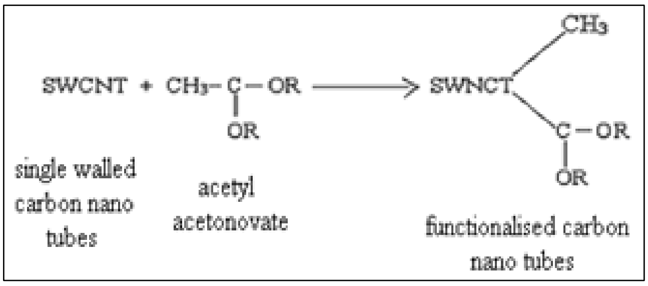
- Micro capsules filled with the curing agent are placed in the composite as shown, with the catalyst placed nearby.
- The catalyst should not come in contact with the curing agent unless cracks are formed.
- When cracks are formed on the surface of the composite, they burst open the microcapsules and the DCPD is released.
- The catalyst polymerizes the curing agent which seals the crack.
- The composite thus obtained has 75% of its original strength.



G. How High Strength is Achieved?

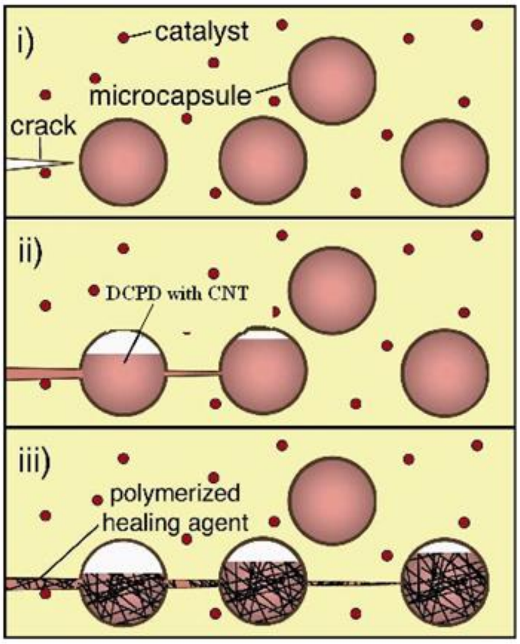
- The strength of the polymer can be increased by the single walled carbon nano tubes (SWCNT) which occupy very less space in the capsule and produce high strength of the composite.
- The problem with SWCNT is the distance belt of fiber elements.
- Fiber distance is of the order of 10 micrometer whereas that of nano tube is 100 nanometer.
- Thus the extremely high volume of nano tubes in the polymer matrix is the major problem.
- This is overcome by functionalizing the CNT with Acetyl acetonovate.
- This leads to the formation of methyl group in the CNT and improves dispersion of CNT in the polymer matrix.
- The functionalized CNT has strong Vander Waal's force of attraction with the DCPD polymerized in the crack.
- As a result of this, the strength of the composite is maintained even after crack is formed and sealed.
- It is observed that the strength increases with temperature. This is an added advantage as the crack tends to propagate which is restricted by this increased strength.

H. Functionalisation process



This functionalised carbon nano tubes (CNT) gets attracted to the polymerised DCPD and then increases the strength of the newly formed crack to around 90%. Thus cracks formed due to impact loads in the aircraft and spacecraft structures no longer appears to be a problem as they are automatically cured by DCPD and further strengthened by CNT so that the propagation of cracks is completely prevented.

I. Process of auto curing



J. Some Practical Applications of Auto Curing

- Electrical system of spacecrafts
- Polymer composite circuit boards
- Bridge supports
- Tennis rackets
- Fuel pipelines in spacecraft

K. Electrical system of spacecrafts

In spacecrafts, there is a need to detect faults before they occur in the electrical systems. Due to abnormal changes in temperature in space the wiring network is found to be greatly damaged. If this happens the whole digital control of space craft crashes. As a result, the spacecraft collapses. Hence it becomes necessary to detect these flaws in the network and repair them before the damage has been done. We can apply this auto curing composite system to achieve this.

L. Polymer composite circuit boards

This is to prevent circuit breaks in breadboards which may result in total collapse of the electronic circuit. Auto curing system may be employed here to automatically seal the cracks before damage by using the appropriate healing agent.

M. Bridge supports

Supports in bridges need to be very strong so that the structure does not collapse due to fatigue. This is achieved by using composites which are auto cured as well as strengthened by carbon nano tubes at these supports to make it more rigid and withstand more dynamic loading.

N. Tennis rackets

Tennis rackets used for playing wear over a period of time. The strings get cut due to excess wear. In order to increase the life of these strings, it can be made of composite strings with CNT technique.

O. Fuel pipelines in spacecraft

Fuel pipelines in spacecrafts need to be designed with utmost care. Because any leaks in them may lead to hazardous effects on the plane. So it is a must to seal cracks when formed immediately. So pipelines might be made of composite auto curing material to seal cracks automatically

III. Conclusion

Thus the auto curing system is helpful in avoiding hazardous situations in spacecrafts greatly and also maintains the composite strength even after crack formation. Researchers are going on in imparting the concept of carbon nano tubes into the composite structures for getting back nearly full strength for the regained composites whose cracks are filled with DCPD. If this concept works well practically we can solve the problem of failure of composites due to impact loading and the life time of composites would be unimaginably increased. Thus the heating of reentry vehicles when it enters the earth atmosphere followed by the cracking of structures due to thermal expansion remains no longer a problem and many astronomers life will be saved!!!!

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