Carbon Fibre Composites using Polyurethanes as Self-healing Agent and Properties Evaluation

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Abstract - *Self-healing polymers are artificial or synthetically-created substances which have the built-in ability to automatically repair damage to themselves. The requirement of self-healing polymers are balance and shelf life, deliverability, reactivity, shrinkage, physical and mechanical, thermal balance and dispersion. Self-healing polymer is made by hand layup technique. In this work carbon fibre is used as a reinforcement, epoxy is used as a healing agent, thermoset phenol formaldehyde is used as a curing agent and polyurethane is used as a self – healing agent. The self-heal composites have been prepared using MFIP resin matrix technology with inbuild self-heal thermoplastic polyurethane resin. Total five composites have been prepared with carbon fibre and thermoplastic polyurethane resin varying from 10% to 30%. These composites were evaluated in terms of mechanical properties, characterization of these composites and selfheal behaviour of these composites. These composites were analysed with mechanical properties, thermal properties, molecular properties, dynamic mechanical analysis and selfheal properties.*

Key Words: Carbon fiber, Epoxy resin, Thermoset phenol formaldehyde, Thermoplastic polyurethane

1. INTRODUCTION

Carbon fiber reinforced composites are used in a wide range of applications in aerospace, mechanical, and civil structures. They have a high strength-to-weight and stiffness-to-weight ratio materials and they have been widely used in many fields such as aircraft, aerospace, ship, etc. Since the CFRP has more advantages than aramid fiber reinforced plastic (AFRP) and glass fiber reinforced plastic (GFRP). Due to the nature of material, most damage in composites, such as delamination, are always barely visible to the naked eye, which makes it difficult to detect and repair. Carbon fiber reinforced composites have numerous advantages over conventional metallic materials, such as light in weight and high strength to weight ratio. Although current non-destructive evaluation (NDE) methods, such as thermography and ultrasonic, are able to detect large barely visible damage in composites, detection of damage precursors, such as micro matrix cracking, is still a challenging research topic.

Self-healing materials exhibit the ability to repair themselves and to recover functionality using the resources inherently available to them. Self-healing can be defined as the ability of a material to heal (recover/repair) damages automatically and autonomously, that is, without any external intervention. Many common terms such as self-repairing, autonomic-healing, and autonomic-repairing are used to define such a property in materials. Incorporation of self-healing properties in manmade materials very often cannot perform the self-healing action without an external trigger. Self-healing materials offer a new route toward safer, longer-lasting products and components. Self-healing materials offer a new route toward safer, longer-lasting products and components.

Composite are multiphase materials which made from a combination of materials of different composition or form, which remain bounded together, but retain their identities and properties without going to any chemical change. A Self-Healing Composite can be achieved by incorporating carbon fiber, epoxy resin, thermoplastic polyurethane resin and thermoset phenol formaldehyde resin

2. Material and Experimental Procedure

Carbon Fiber was purchased from Adorn Engineer, Epoxy Resin was purchased from Atul Ltd, Thermoplastic Polyurethane Resin was purchased from Western Pu Industries and Thermoset Phenol Formaldehyde Resin was purchased from Tipco Ltd. As given in Table 1

Table 1: Source and Grade of Material

Carbon Fiber	Epoxy Resin	Thermoplastic Polyurethane Resin	Thermoset Phenol Formaldehyde Resin
Source: Adorn Engineer	Source: Atul Ltd Mumbai	Source: Western Pu Industries	Source: Tipco Industries Ltd Valsad
Grade: 12 K / 400 gsm	Grade: Lapox B-11	Grade: 2710	Grade: Tpf/W/1617

2.1 Methodology

2.2.1 Hand Lay Up Techniques

The composite sample were made with the help of hand layup technique. The composition of making the composite sample tabulated in Table 2.

Table 2: Composition of Composites

S. No	Carbon Fiber (gm)	Epoxy %	PU %	Epoxy (gm)	PU (gm)	PF (gm)
P-1	148	90	10	67.5	7.5	25
P-2	148	85	15	63.75	11.25	25
P-3	148	80	20	60	15	25
P-4	148	75	25	56.25	18.75	25
P-5	148	70	30	52.5	22.5	25

2.2.2 Compression Moulding

The curing of the composite sheet were done with the help of compression moulding machine in processing department OLC CIPET Ahmedabad. Five composite sheet is to be curried.

2.2.3 Contour Cutter

Contour cutter used to finish the composite sample in dumbell and rectangular shape. The finishing was done in HLC CIPET Ahmedabad.

3. RESULT AND DISCUSSION

3.1 FTIR Analysis

FTIR is a wonderful analytical tool for screening as well as profiling the different types of polymer samples. There are various types of chemical bond in a molecule, FTIR identifies those bonds in a molecule via producing an infrared absorption spectrum. The resulting spectra produces a profile of the sample, a special molecular fingerprint that can be used to without problem screened and scan the samples for many specific components. FTIR is an nice analytical instrument for detecting chemical bond and characterizing covalent bonding information. FTIR analytical testing and records interpretation for polymers are handy globally.

In order to facilitate the study of quantitative conversion of the resin to the intermediate adduct, FTIR analysis has been chosen here. The FTIR spectrum of five samples P1 to P5 are presented in Figure 1 to 5.

It is very clearly observed that 1735 cm-1 peak is designated for >C=O peak for polyurethanes. As the concentration increase of polyurethanes peak of -N-C=O observed at 2280 cm-1 in case of P2 to P5 composite samples which clearly indicated that the composites samples after curing polyurethanes remain suspended in the resin matrix and does not take part in the curing reaction. These

polyurethanes will act as thermoplastic and will give the glass transition temperature at 54°C which act as self-healing substances. On crack observed for the composite samples on reheating of composite these polyurethanes will change the phase and fill the matrix where the crack created and that how these resin matrices is working on reheating.

The intensity of peak of -N-C=O at 2280 cm-1 increased on increase of the polyurethanes content from 10% to 30% and this proved that these polyurethanes remain self-healing agent in the resin matrix of these composites.
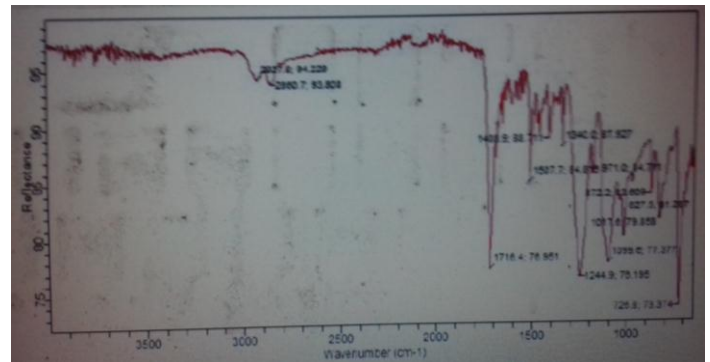

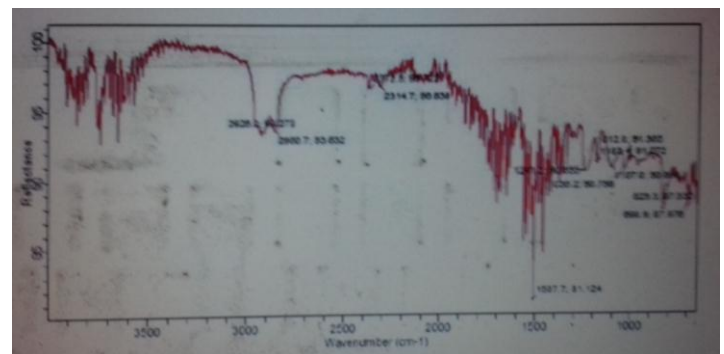**Figure 1** FTIR Result of Composite P 1
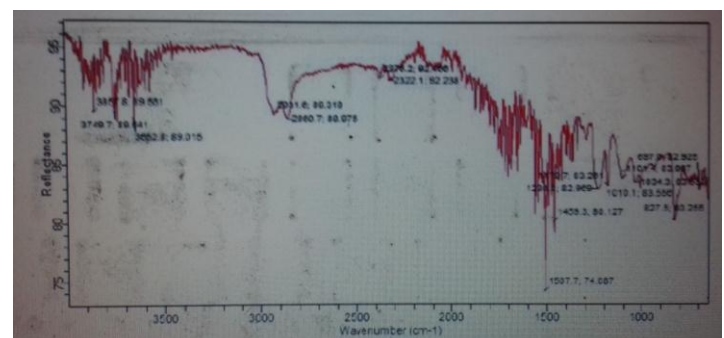

Figure -2 FTIR Result of Composite P 2

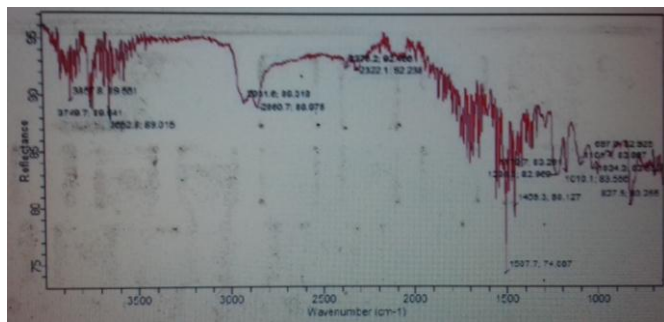**Figure -3** FTIR Result of Composite P 3

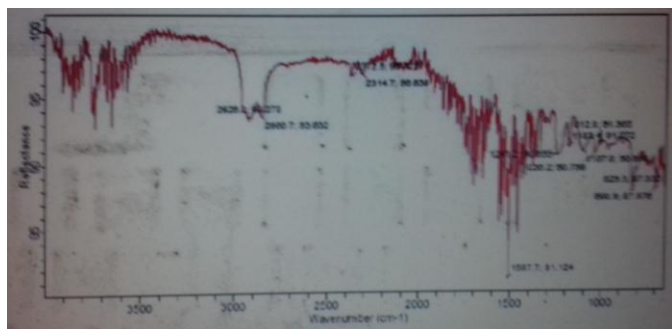**Figure -4** FTIR Result of Composite P 4

Figure -5 FTIR Result of Composite P 5

3.2 DSC Analysis

Figure 6 shows the DSC thermograms following cure and post-cure. The average DSC Tg values from neat epoxy were calculated to be 119°C, while the average PU content of 25 to 30 wt%. More importantly, DSC showed that the addition of 10 to 20 wt% PU did not significantly alter the cure, and the lack of an exothermic peak in the curves implied that the composites were fully cured.

The sample containing PU from 10-20 wt% does not showed any Tg values as these thermoplastic materials does not give significant effect on matrix of epoxy and phenolic matrix. But in case of P4 and P5 samples where the PU content is significantly higher 25 to 30% showing the glass transition temperature of 119°C temperature showing these material will work as self-healing material under reheating and restress condition.
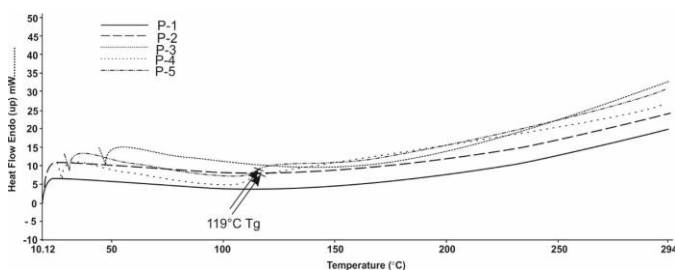

Figure -6: DSC results of composites samples from P1 to P5

3.3 TGA Analysis

Pyris TGA, temperature rise from 50°C to 850°C and rate of rise 20°C /min is used to determine the degradation pattern of resin matrix. On comparison it was found that sample P3 to P5 degrading with two step mechanisms as shown in Figure 7. The first step degradation indicates degradation of thermoplastic Polyurethanes resin which actually doesn't cure and does not acted as part and parcel of cured resin. Further the sample degrade which indicate the degradation of cured resin, where as other samples P1 and P2 showing single step degradation which again proves that the sample containing thermoplastic polyurethanes resin acted as self-heal polymer. This thermoplastic material suspended in cross linked structure of EP- Phenolic resin .
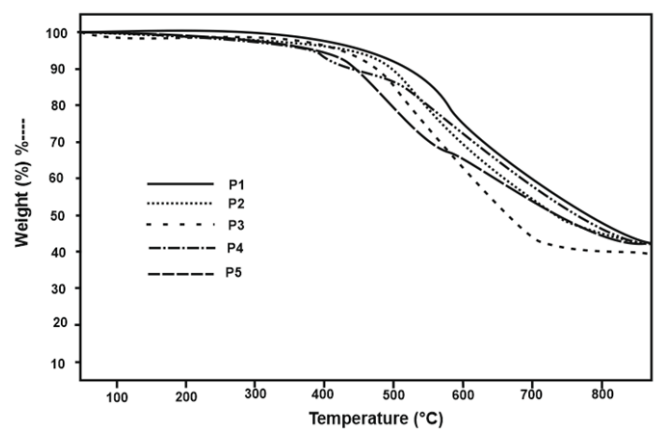

Figure -7: TGA results of composites samples from P1 to P5

3.4 DMA Analysis

The self-heal effects of thermally responsive composites were quantitatively analyzed using DMA. Figure 8 showed the self-heal behavior of PU- epoxy composites (sample P4 and 5) undergoing four cycles of temperature changes above and below the transition temperatures. The graph displayed that the differences in deformation strains of the neat epoxy composites were larger when heating between 150-185°C compared to the other temperature ranges. On the other hand, it was observed that the differences in deformation strain between 150-185°C became less noticeable as the neat epoxy composites was exposed to more cycles (P1). Four cycles of shape memory behavior in PU-epoxy selfheal composites (Sample P4 an P5) are shown in Figure 8. The self-heal composite samples possessed a higher strain deformation and lower stress compared to the neat epoxy composites. The higher strain and reduced stress values may have been attributed to graphene sheets serving more as a resin tougher rather than resin reinforcement.
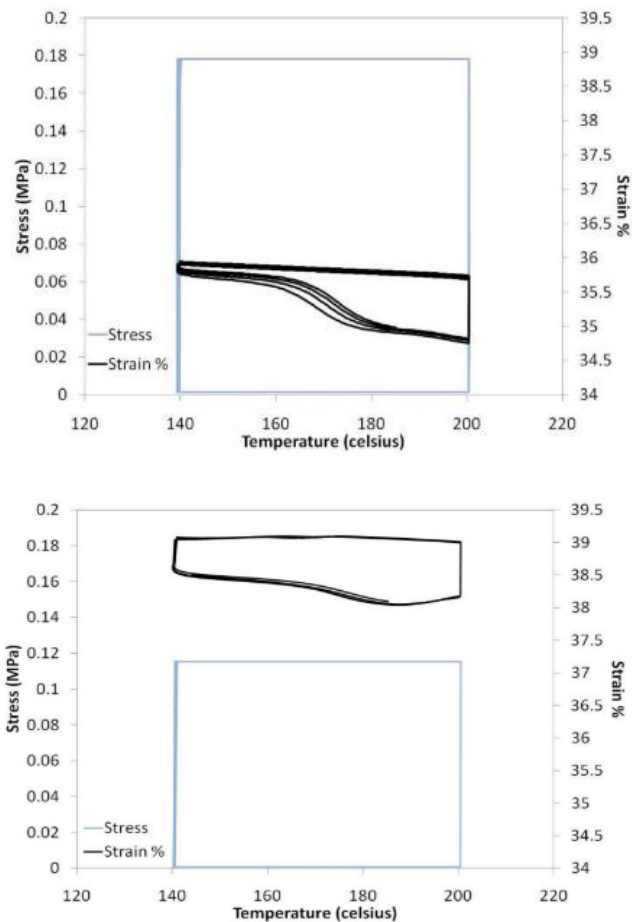
Figure -8: DMA results of composites samples from P1 to P5

3.5 Optical Microscope

A simple microscope is a microscope that uses only one lens for magnification, and is the original light microscope .Van Leeuwenhoek's microscopes consisted of a single, small, convex lens mounted on a plate with a mechanism to hold the material to be examined)the sample or specimen .(Demonstrations by British microscopes Brian J .Ford have produced surprisingly detailed images from such basic instruments .The use of a single, convex lens to magnify objects for viewing is found today only in the magnifying glass, the hand-lens. The optical photographs of self-healing composite are depicted in Figure 9.
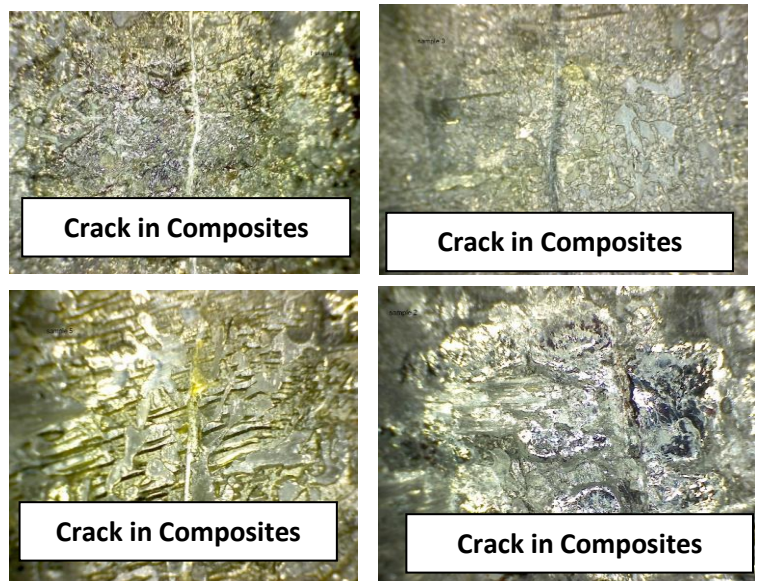

Figure -9: Optical Micrographs of composites from P1 to P5

3.6 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces image of a sample by scanning it with a focused beam of electrons .The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information out the sample surface topography and composition .The electron beam is generally scanned in a raster scan pattern, and the beam position is combined with the detected signals to produce an image SEM can achieve resolution better than 1 nanometre .Specimens can be observed in high vacuum, in low vacuum, in wet conditions and at a wide range of cryogenic or elevated temperatures as given in Figure 10.
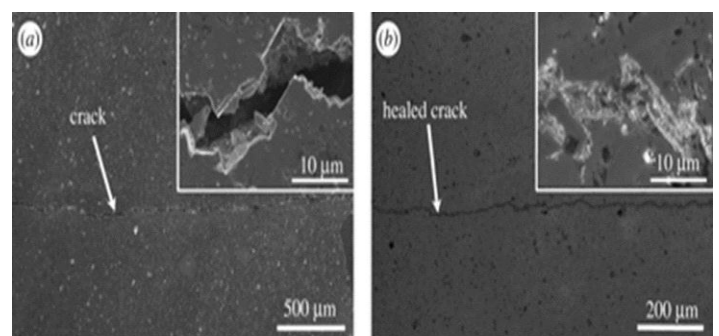

Figure10: SEM Photographs of Self-Healing Composites.

PUs containing a soft block with a glass transition instead of a semi-crystalline soft bock. The glass transition could be tuned between 50 and 65 ∘C. Moreover, specimen with complex forms based on PUs with a thermoplastic elastomeric and shape memory behavior could be obtained by the polymerization of 1,3-butanediol and hexamethylene diisocyanate for the soft block as well as 4,4'-bis-(6-hydroxy hex- oxy) biphenyl and toluene 2,4-diisocyanate for the hard block The glass transition temperature of the soft segment was around 30∘C. The utilization of crosslinked polyester type PUs enabled a tuning of the switching temperature between 0 and 60∘C Classical thermoplastic elastomers like PUs feature an excellent processability. However, the missing chemical crosslinks lead to inferior properties compared with covalently crosslinked polymers. Latter materials show higher recovery stresses and higher cyclic recoverable strains. Therefore, crosslink- able PU systems have been investigated. The crosslinking was achieved by the introduction of double bond containing monomers and subsequent electron beam treatment.

4. Mechanical properties evaluation of carbon fibre composites

The mechanical properties, among all the properties are often the most important properties because virtually all service condition and the majority of end-use applications involve some degree of mechanical loading.

4.1 Tensile Strength

Tensile elongation and Tensile modulus dimension are amongst the most necessary indication of a power in a composite and are the most widely targeted houses of plastic materials. Tensile strength is given in Table 3, in a wide sense, is a dimension of potential of a cloth to stand up to forces that have a tendency to pull it apart and to decide in what lengthen the fabrics stretches earlier than breaking.

Tensile Strength at Break= Load Recorded at Break/ Cross Section Area

Table 3: Tensile Strength of carbon Fibre – PU-Epoxy composites

Sample Design ation	Area (mm2)	Breaking Load (KN)	Tensile at Break (MPa)
P1	50	1475.96	29.51
P2	50	1477.00	42.14
P3	50	1478.30	56.12
P4	50	1480.20	58.34
P5	50	1496.21	60.03

It is clearly observed that on increase of PU in Epoxy-Carbon Fibre composites, the tensile strength is also increase which indicate that Polyurethane not only act as self-healing agent but also increase the strength of the composite material. The composite sample from P3 to P5 the value is almost same on increasing order as shown in Figure 11. On increase of polyurethanes, surprisingly the tensile values were also increase could be creasing to thermoplastic polyurethanes acts as reinforcing material and on increase of this content the values showing in increasing trends.
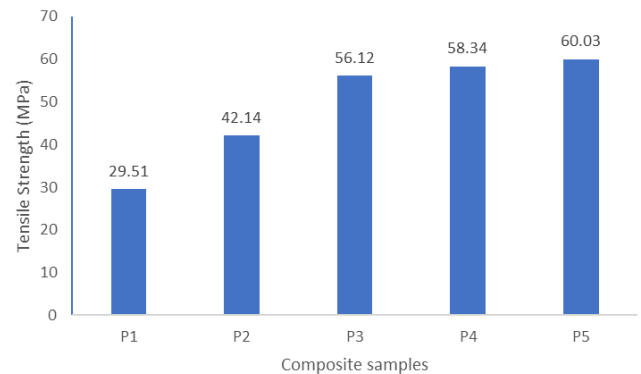

Figure 11: Comparative Tensile Strength for Carbon -PU-Epoxy composites

4.2 Flexural Strength of carbon Fibre – PU-Epoxy composites

As it was expected from tensile strength values there is increase in flexural strength values along with the flexural modulus values which once again confirmed that these polyurethane suspended molecules act as reinforcing materials and act as nanowhisker. These nanowhsker fibre on increase in the percentage there is increase in flexural strength as well as flexural modulus values as illustrated in Table 4.

Table 4: Flexural Strength of carbon Fibre – PU-Epoxy composites

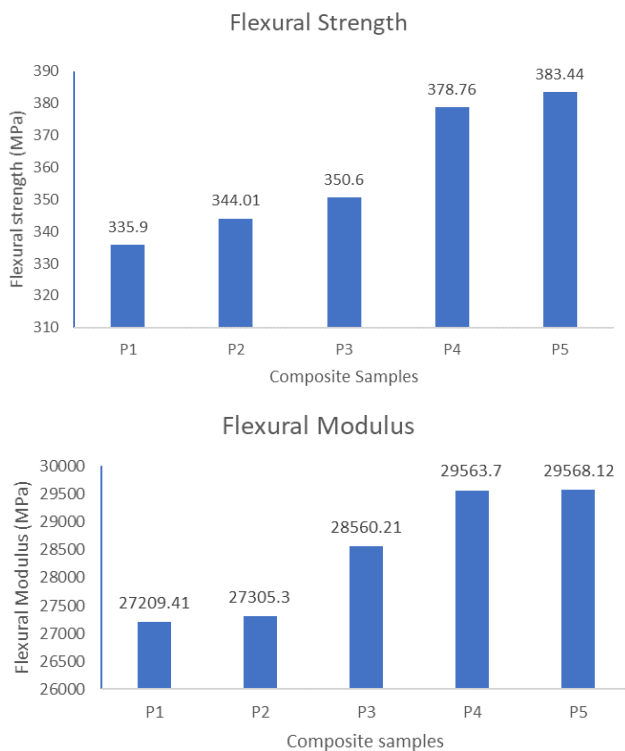| Sample Designation	Flexural Strength (MPa)	Flexural Modulus (MPa)
P1	335.90	27209.41
P2	344.01	27305.3
P3	350.60	28560.21
P4	378.76	29563.7
P5	383.44	29568.12

Flexural Strength

Flexural Modulus

Figure 12: Comparative Flexural Strength and Flexural Modulus for Carbon -PU- Epoxy composites

4.3 Impact Strength

Izod Impact Testing is an ASTM trendy technique of deciding the have an impact on resistance of material. A pivoting arm is raised to precise height and then released. The arm swing down hitting a notched sample, breaking the specimen. The power absorbed with the aid of the pattern is calculated from the peak the arm swing to after the hitting the sample. The notched pattern is generally used to decide influence power and notch sensitivity. The values given in Table 5.

Table 5: Impact Strength of carbon Fibre – PU-Epoxy composites

Sample Designation	Thickness (mm)	Scale Reading	Scale/ Thickness (J/m)
P1	3.64	7.49	2057
P2	3.49	7.45	2134
P3	3.40	7.48	2200
P4	3.15	7.49	2385
P5	3.18	7.52	2364

Apart from tensile and flexural impact strength values are also showing the increase of polyurethanes there is increase in impact strength from P1 to P4 and there is slight decrease in impact strength values for composites sample P5. The increase in impact strength is depicted in Figure 13. The increase can be visibly seen from Figure 33 and it is continuously increased from sample P1 t P5 as Polyurethanes increase.
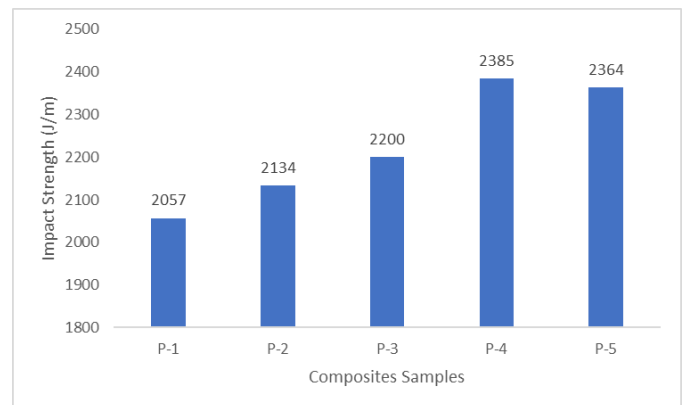

Figure 13: Impact Strength and Flexural Modulus for Carbon -PU- Epoxy composites

5. CONCLUSIONS

Self-Healing Mechanism of Polyurethanes as Self-Healing agent

The system was based on a binary polymer blend from two different multiblock copolymers, whereby the first polymer component was providing the segments forming hard domains and the second the segments forming the switching domains. When the switching segment is crystallizable, the amorphous polymer network will become semi crystalline in its temporary shape and will consist of two different phases. The polymer network displayed in Figure 14.
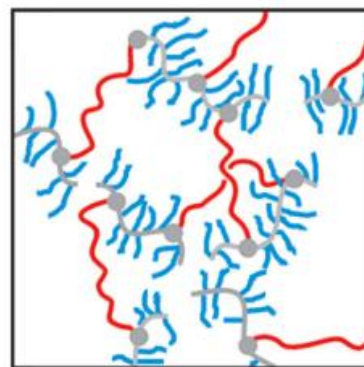

Figure 14: Polyurethanes act as nano whisker and self-healing polymer

The polyurethane networks prepared by the prepolymer method using MFIP Technique, which provided the switching segment, and a diisocyanate and polyol, which provided the covalent crosslinks. Physical crosslinking occurs on cooling by solidification of switching domains, e.g., by vitrification or crystallization. By reheating, the crystallites will melt or the glassy domains will return to the viscous state. Chemical crosslinks are formed by reaction of two functional groups under formation of a chemical bond. This chemical bond can be cleaved on demand and both segments can act as switching segment and are capable of stabilizing the temporary shape by aggregation and solidification if the formed physical net points have sufficient strength to block the entropy driven elastic recovery. Furthermore, it must be noted that the segments providing the switching domains and the net points, which determine the permanent shape, do not have to be covalently connected to each other. On increase of polyurethanes the storage modulus of the rubbery plateau was significantly increased with increasing ionomer content. Besides chemical modification, the processing had a significant effect on the shape-memory properties of polyurethanes.

Covalently crosslinked IPN were realized by combination of polymerization and polyaddition reactions. Generally, such IPN are prepared in the order polyaddition first and polymerization reaction second.

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