

Preparation of PMR+PAN Resin Matrix and its Studies on Carbon Fiber Reinforced Composite: Hydraulic, Chemical, and Temperature Stability

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ABSTRACT: PMR is widely used as high temperature resin for advanced composite materials in application above 312°C. The cured PMR+PAN resin displays the best overall balance of processing behavior, thermo-oxidative resistance with improved mechanical performance at 330°C. Polyacrylonitrile (PAN) was used as modifier within polymerisable monomer reactant (PMR) in an ultra low concentration (10^{-4} , 10^{-3} , 10^{-2} , and $10^{-1}\%$) through critical crosslinking concentration (CCC). This produces PMR, as a new material due to *in situ* generation of ladder structure and an emanation of PAN fiber within PMR Matrix. AFM tomography shows clear evidence of

it. The lamina of this type of material enhances the adhesion properties within the carbon fiber. The physico-chemical properties are much better than the normal PMR. The newly developed materials in the form of cured resin (pellets) and carbon fiber reinforced composite shows minimization of moisture and chemical stability with temperature resistivity including better mechanical properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2007

Keywords: PMR; PAN; *in situ* generated; ladder structure; emanation and laminate

INTRODUCTION

Hydraulic and chemical stability with temperature resistance is one of the important research parameter in resins and composites, which generally affect the mechanical performance of the material.^{1–3} The present paper reports the preparation of resin by incorporating polyacrylonitrile (PAN) in ultra low concentration within the polymerisable monomer reactant (PMR) which drastically improves the mechanical properties of PMR resin. Further, it is used as laminate on carbon fiber as a matrix. PMR is a class of high temperature resistant addition polyamide, which is a 'Nadic end capped addition polyamide of BTDA and MDA'. This class of polyamide has emerged as a powerful polymer matrix in carbon fiber reinforced composite as it possess an excellent combination of thermal (312°C) and mechanical properties.^{4–10} However, PMR and other currently available resin suffer from processability, hydraulic and chemical instability, and thermal resistivity.

PAN is the material, which possesses all the ingredients necessary for conversion into fibers. PAN can

be easily spun into highly oriented chains along the fiber axis, which forms the basis for the ultimate structure to be formed. PAN decomposes before melting and it becomes plastic at about 180°C, and thus can be stretched at this stage to further improve upon the orientation of molecular chains. PAN is also reported to be a semicrystalline vinylic homopolymer^{11–13} and good resistive polymeric material with adhesive fibrous behavior. PAN is also widely used for making membrane and offers good resistance and shows good mechanical strength and thermal stability.^{14,15} Taking this into account authors have incorporated PAN in PMR to form resin and achieve synergistic properties. PAN has been incorporated in an ultra low concentration in PMR matrix, through critical crosslinking concentration (CCC), to enhance the properties. Further, this developed polymeric resin (PMR+PAN) is used as laminate on carbon fiber to prepare carbon fiber reinforced composite with improved hydraulic and chemical stability, and thermal resistiveness along with better mechanical performance. The hydraulic characteristic of prepared resin has been evaluated by constructing water absorption isotherms, which involves soaking for 24 h and maximum 120 h. The temperature resistivity of resin and composite was determined by thermogravimetric analyzer. Polar and nonpolar solvents were taken to observe the effect of chemical stability.

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The purpose of using polymeric resin as a lamina on carbon fiber is to bind the fiber together by virtue of its cohesive and adhesive characteristics. This transfers the load through the fibers, which protects them from environment and handling. Also this keeps the reinforcing fibers in the proper orientation and position so that they can bear the indented load. The polymeric resin generally determines the overall service temperature limitations of the composite and also controls its environmental resistance (hydraulic and chemical). Polymeric resin (PMR+PAN) plays an important role in improving the weatherability, temperature, and chemical resistivity of the fiber composite, with better mechanical properties to be used under different conditions such as marine environment, aerospace, etc. In addition to this, Atomic force microscopy has been utilized to provide microscopic evidence of fiber formation within the PMR matrix.

EXPERIMENTAL

Material used

Nadic end capped oligomeric amic acid (NECOAA), an addition product of Benzophenone-3, 3', 4, 4'-Tetracarboxylic dianhydride (BTDA) and 4, 4'-Methylene dianiline (MDA) end capped by N-oxyl anhydride was prepared by MRC's proprietary method and chemical used were supplied by MRC, Vadodra, India. NECOAA having formulated molecular weight of 1500 and stored at -10°C in airtight container for further use. Analytical grade polyacrylonitrile (PAN) was supplied by M/S Indian Petrochemicals Corp., Vadodra.

The high grade dimethylacetamide (DMAc), Methanol, Acetone, Toluene, Xylene, Ethanol, and Diethylene glycol were supplied by E-Merck (Germany) and were used as received due to their high purity (over 99%). Doubled distilled deionized water was used to characterize hydrolytic stability. High modulus carbon fiber has been used to prepare composite, which was supplied by DRDL, Hyderabad, India.

Preparation of NECOAA+PAN matrix

PAN (which is in powder form) was dissolved in a known volume of DMAc. The calculated quantity (CCC of 10^{-4} , 10^{-3} , 10^{-2} , and $10^{-1}\%$ w/w) of PAN solution was incorporated in NECOAA. The various compositions as well as unmodified NECOAA (NECOAA without PAN) were spread over clean and dry glass plate by means of circular glass rod so as to obtain uniform films of 50 ± 2 micron thickness. These films were subjected to two stepped curing process to first convert them into oligomeric imide (NECOI) and secondly into crosslinking

(PAN+NECOI) films. The curing cycle comprises of 90°C for 24 h and thereafter, half hour each at 110, 130, and 150°C for first step, which partially imidizes the reactant. The dried films were cured into fine powder and then the powder was placed into a rectangular metal dye cavity at room temperature. The dye was pressed and heated in steps from 90 to 300°C for 15 min (at the interval of 20°C) and it was cured at 330°C for 1 h (the pressure of 7.2 MPa was applied on the dye in the later half hour) and then dye was allowed to cool slowly to room temperature without any applied pressure. The molding (in the form of pellets) was removed from the dye and the yielded product was further characterized.

Laminate of PMR+PAN matrix on carbon fiber

The received carbon fiber was desized with acetone and thereafter carbon fiber was heated to the temperature of 20°C . This resultant carbon fiber was used to form laminate. Further, NECOAA+PAN at different CCC (10^{-4} , 10^{-3} , 10^{-2} , and $10^{-1}\%$) were coated on carbon fiber. Prepregs of carbon fiber were prepared in which the ratio of carbon fiber was 65 and resin was used. A calculated quantity of uniformly mixed resin at different CCC was coated on desized carbon fiber and was heated from 90 to 150°C for half hour (interval of 20°C) in heavy-duty oven. The resultant prepregs of carbon fiber were stacked in sufficient number to build up the composite with thickness from 6 to 8 mm. The stacked prepregs were kept in 3-piece leaky mold, to which pressure was applied. The time-temperature profile for curing at temperature ranging from 90 to 300°C (at the interval of 20°C) for 15 min and 330°C for 1 h. The mold was brought to room temperature for removal of the sample. The yielded product was in the form of carbon fiber reinforced composite.

CHARACTERIZATION

Soxlet test

Soxlet test was used for the extraction of solvent from the resin (NECOI+PAN) and carbon fiber composite, for this a standardized soxlet apparatus was used. A $20 \times 20 \text{ mm}^2$ and $30 \times 32 \text{ mm}^2$ sized specimen was cut from the 20 mm-thick pellets and 8 mm-thick composite. Further, these samples were placed in soxlet cavity (filled with toluene) then it was heated gently to evaporate toluene, which after condensation comes in contact with the sample. This process leaches out the solvent from the samples. The process is repeated for 2 h, so that maximum solvent is leached out and at 330°C , cured resin and

carbon fiber composite solvent extraction was found to be nil.

Hydraulic test

The water absorption characteristic of polymeric materials mainly depends on the composition of the material and moisture cannot be ignored since a small amount of moisture can alter the key properties.

For water absorption test, samples of resin and carbon fiber were cut and conditioned at 110°C for 2 h. Conditioned samples were weighed on Perkin-Elmer electronic balance model AD4 with an accuracy of 0.0001 g. Weight was designated as W_1 . Five samples of each composition were dipped in methanol for various durations from 24 to 120 h in the interval of 24 h at $(23 \pm 1)^\circ\text{C}$. After the test period, samples were removed from methanol and weighed again. This is referred to as wet weight (W_2) of the samples. These samples were reconditioned for another 2 h at 110°C and weighed again. This weight is referred as (W_3). Finally, reconditioned samples were immersed in double distilled water until equilibrium condition is reached. Weight of these wet samples were taken at regular intervals and designated as (W_4). Calculations were carried out as follows:

Percentage increase in weight during curing = $\frac{W_2 - W_1}{W_1} \times 100$

Percentage soluble matter lost in methanol = $\frac{W_2 - W_3}{W_3} \times 100$

Percentage water absorption = $\frac{W_4 - W_3}{W_3} \times 100$

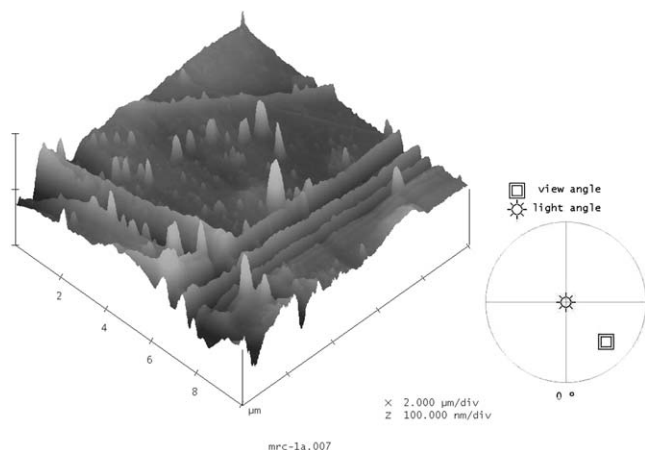


Figure 1 3D topography of PMR + PAN resin.

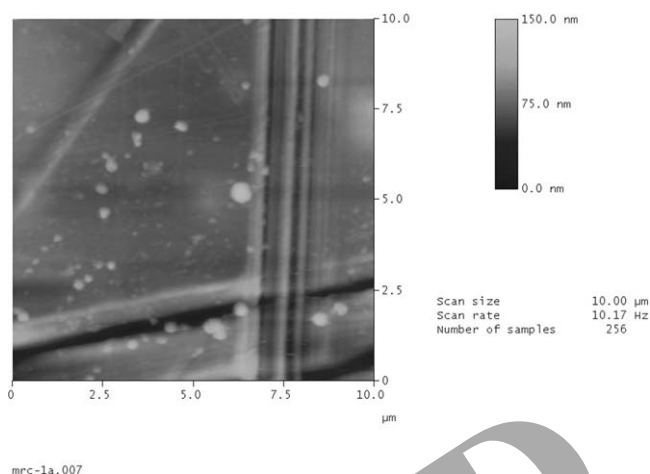


Figure 2 2D topography of PMR + PAN resin.

Chemical test

For chemical test, authors have utilized one polar (ethanol) and one non polar (xylene) solvent. The cured resin and composite specimens were made to dry at 110°C by keeping it in an oven. Thereafter, the specimens were dipped in container filled with ethanol and xylene for various durations from 24 to 120 h in the interval of 24 h. Further, absorption was calculated by the method explained above.

Dynamic thermogravimetric analysis

Dynamic thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 instrument using pyris software. The heating rate was 10°C/min in air and nitrogen atmosphere.

Mechanical test

Mechanical strength of the composite samples of size $(1 \times 15) \text{ cm}^2$ were carried out according to ASTM D-882 standard method. Crosshead speed was

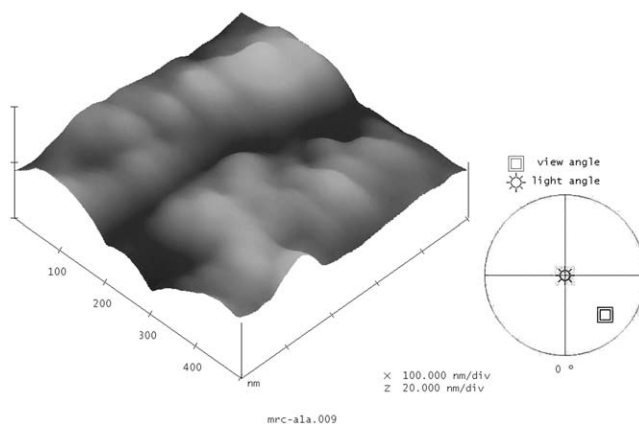


Figure 3 3D topography of pure PMR.

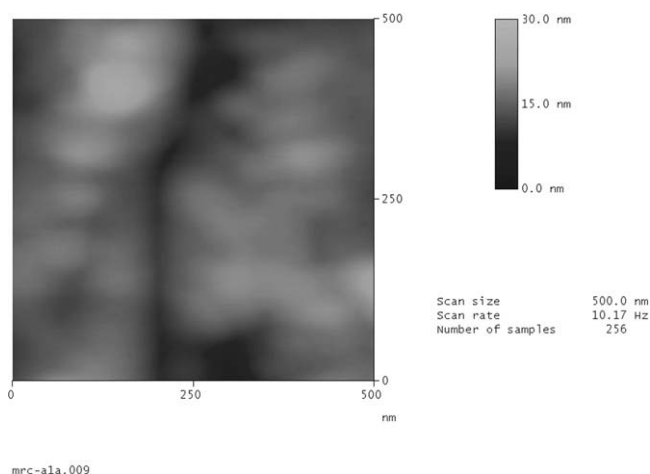


Figure 4 2D topography of pure PMR.

maintained at 5 mm/min at room temperature. The samples were conditioned at 110°C for 24 h before the testing.

Determination of tensile strength, modulus and elongation

The tensile tests were conducted at room temperature on an Instron Universal Testing machine (Model No. 4302) according to ASTM test method No. D-638. The tests were made on rectangular samples. The crosshead speed (initial strain rate) was 5 mm/min and grip length 80 mm in each case. Five samples were tested and the average value was considered. The following parameters have been computed using the stress-strain curve:

Tensile strength: the tensile strength was taken as the stress at break.

Elongation at break: the elongation at break or the strain at break was taken as the strain when the sample failed.

Determination of flexural strength and modulus

Flexural strength of the composites was determined according to ASTM D-790 using Instron Testing

Machine (model no. 4302) and three point loading system utilizing the center loading on a supported beam (width = 13–14mm).

The test parameters employed were as follows:

Support span – to – depth ratio = 32 : 1

Cross head speed = 10 mm/min

Chart speed = 200 mm/min

The test specimens were cut from the composites by diamond wheel cutter and sides were polished. In each case, at least five samples were tested and the average value was considered.

The flexural strength was then calculated using the following relation: flexural strength = $3PL/3bd^2$, where, P , maximum load; L , support span length; B , width of the specimens; and D , depth (thickness of the specimens).

Flexural modulus was calculated using the following relation: flexural modulus = $L3m/\Delta^2$, where, m , slope of the tangent to the initial straight-line portion of the load deflection curve.

Atomic force microscopy

AFM topography of samples were imaged using (Digital Instruments) in contact mode.

RESULTS AND DISCUSSION

Major constituents used in forming composite materials are fiber particles, laminates or layer, flakes, and fillers, which are known as reinforcing materials. To improve the strength of a composite, the reinforcement must be stronger and stiffer than the matrix, and it must modify the failure mechanism in an advantageous way. In present work, polyacrylonitrile has been used as a modifier in NECOI to compact its structure. PAN is a fibrous material^{16,17} and at 250 and 300°C it is cyclised to form ladder type structure. In view of this authors have studied the PAN chemistry up to 330°C with PMR resin environment; the result shows good agreement with our assumption. When NECOAA interacts with PAN and forms a strong chemical bonding, which is totally different and better than neat NECOAA. The

TABLE I
Hydraulic and Chemical Sorption for Pellets of Pure PMR and Varying PAN with Different Critical Crosslinking Concentration in NECOAA Matrix at 330°C Curing Temperature

S. no.	Sample designation of resin	Chemical absorption					
		Water absorption (%)		(%)(Ethanol)		(%)(Toluene)	
		24 (h)	M_x (h)	24 (h)	M_x (h)	24 (h)	M_x (h)
1.	Pure PMR	1.42	1.87	2.76	4.18	2.88	5.20
2.	(PMR + PAN) 10^{-4}	1.29	1.66	2.44	3.87	2.79	5.01
3.	(PMR + PAN) 10^{-3}	1.31	1.55	2.33	3.76	2.67	4.93
4.	(PMR + PAN) 10^{-2}	0.76	1.44	1.98	2.54	2.05	3.87
5.	(PMR + PAN) 10^{-1}	1.24	1.77	2.55	3.17	2.67	4.81

TABLE II
TGA Derived Parameters for Pellets of Pure PMR and Varying PAN in Different Critical Crosslinking Concentration in NECOAA Matrix

S. no.	Sample designation of resin	TGA parameter	
		$D_{0.5}$ (°C)	Residue (%)
1.	Pure PMR	478.15	56.38
2.	(PMR + PAN) 10^{-4}	481.48	56.11
3.	(PMR + PAN) 10^{-3}	482.03	57.69
4.	(PMR + PAN) 10^{-2}	490.73	61.23
5.	(PMR + PAN) 10^{-1}	482.31	58.75

cyclization of PAN at 330°C provides flexibility and rigidity within NECOI+PAN resin.

One of the most important feature of present research work is the incorporation of PAN that is in ultra low concentration 10^{-4} , 10^{-3} , 10^{-2} , and 10^{-1} % with PMR through CCC, which drastically enhances the mechanical strength including adhesiveness, hydrolic and chemical stability with temperature resistivity. This novel approach of mixing one material in ultra low concentration with the other, completely changes the properties of the material.

It has been established¹⁸⁻²⁰ that the lower concentration results in reaction product of oligomeric amide acid and modifies at micro- and nanodimension. As PAN is modifier, it gives an emanation of PAN fiber within PMR matrix. Figures 1 and 2 show 3D and 2D topography of PMR+PAN resin at 10⁻⁴ CCC, which provide a clear evidence of emanation of PAN fiber within the PMR matrix in comparison to neat PMR (Figs. 3 and 4), where only plain morphology is observed. This emanated PAN fiber showing all the characteristics of developed fiber which strengthens the matrix from inside a molecular level and also provides better stability within the matrix as the temperature increases (characterized up to 330°C). PAN behaves like fiber between PMR matrix to give synergistic properties with better crosslinking.

In the light of sensitivity of polyamide towards moisture, several researchers have studied its hydraulic nature and have tried to reduce the moisture

uptake, so as to retain its desirable attributes. The effect of incorporating low concentration of organic crosslinker or modifier in polyamide matrix results in reduced absorption characteristic.^{21,22} Thus emanation of PAN fiber in NECOI assesses its suitability for desired applications.

Hydraulic and chemical analysis

Physicochemical properties depend upon interaction between the filler and the matrix. A resin consisting of NECOAA+PAN matrix and its laminate on carbon fiber fulfills these requirements to a greater extent. Table I, shows the hydraulic and chemical absorption of pure NECOI and NECOI+PAN resin. Minimum absorption is observed at 10⁻⁴% crosslinker stage, where the emanation of fiber within the NECOI matrix is more eminent. Being in liquid form, NECOAA+PAN resin can penetrate deep into the pores of the carbon fiber and can form a chemical bond with the carbon moieties present within as well as on the surface of the carbon fiber. This interaction of the resin and carbon fiber is critical in determining the properties, especially hydraulic and chemical stability with temperature resistance of the composite material; it is expected that the strong covalent bonding may appear during the cure reaction of the matrix on the carbon fiber. The hydraulic and chemical uptake values of carbon fiber composite with pure NECOI and varying PAN at different CCC are given in Table III, PAN incorporated specimens show less hydraulic absorption and at 10⁻²% CCC, absorption is found to be minimum. Lower absorption in case of composite may be attributed to the presence of PAN as a modifier in PMR resin. Available free volume of polymeric matrix gets filled by PAN fiber and thus making them not available for water molecules and also for polar or nonpolar solvent molecules.

Temperature resistivity

Main interest to study the temperature resistivity is to evaluate the strength of the resin and composite,

TABLE III
Hydraulic and Chemical Sorption for Carbon Fiber Composite by Pure PMR and with Varying PAN with Different Critical Crosslinking Concentration in NECOAA Matrix at 330°C Curing Temperature

S. no.	Sample designation of composite	Water absorption (%)		Chemical absorption (%)			
		Water absorption (%)		(%) (Ethanol)		(%) (Toluene)	
		24 (h)	M_x (h)	24 (h)	M_x (h)	24 (h)	M_x (h)
1.	CF + Pure PMR	1.91	2.43	2.98	5.19	3.15	6.20
2.	(CF + PMR + PAN) 10^{-4}	1.60	2.19	2.71	5.04	3.05	5.86
3.	(CF + PMR + PAN) 10^{-3}	1.58	2.12	2.57	4.75	3.07	5.85
4.	(CF + PMR + PAN) 10^{-2}	1.30	1.07	2.27	4.18	2.97	4.81
5.	(CF + PMR + PAN) 10^{-1}	1.52	2.07	2.63	4.82	3.01	5.25

CF, Carbon fiber.

TABLE IV
TGA Derived Parameters of Pure Carbon Fiber, Composite of Pure PMR on Carbon Fiber and Varying PAN with Different Critical Crosslinking Concentration in NECOAA Matrix

S. no.	Sample designation of composite	Temperature of 10 % ($D_{0.1} T$) ($^{\circ}C$)	IDT		$D_{1/2} T$ ($^{\circ}C$)	UDT ($^{\circ}C$)	Residue content (%)
			Ist step	IInd step			
1.	Carbon fiber	560	579	–	712.2	743.2	52.14
2.	CF + PMR resin	478.15	441	–	488.15	603.05	56.38
3.	(CF + PMR + PAN) 10^{-4}	479.8	401.5	677.6	722.5	723.9	58.33
4.	(CF + PMR + PAN) 10^{-3}	508	395.3	614.9	722.9	729.3	61.47
5.	(CF + PMR + PAN) 10^{-2}	511	485.1	691.4	717.0	733.4	62.83
6.	(CF + PMR + PAN) 10^{-1}	481.3	453.7	685.5	705.6	717.7	60.91

CF, Carbon fiber.

which is developed by incorporating the PAN within the PMR matrix. In comparison to pure PMR, when PAN is incorporated and cured at evaluated temperature, $330^{\circ}C$, it forms a ladder structure within resin due to emanation of PAN fiber in PMR matrix, which increases the strength of the matrix as a whole which is reported in Table V. Table II, shows the TGA derived parameters on pellets of pure PMR and NECOI+PAN at different CCC and Table IV shows the TGA parameters of pure carbon fiber, pure PMR and laminated NECOI+PAN matrix at different CCC on carbon fiber. Increase in decomposition temperature and maximum residue content was found for NECOI+PAN at $10^{-2}\%$ CCC in respect to pure NECOI. This also shows the development of PAN fiber within the resin and with the increase in temperature the fiber gets further strengthened and thereby strengthens the resin.

Mechanical analysis

Mechanical properties of any polymeric system depend on the orientation of macromolecular segments and amount of crosslinking between the macromolecular units. Tensile properties are basically characterized by measuring stress at break; yield stress and corresponding elongation as a function of polymer composition. Tensile modulus is one of the important small strain mechanical property. It is the key

indicator of the stiffness or rigidity of the material and quantifies the resistance of the specimen to mechanical deformation in the limit of infinitesimally small deformation. Modulus of any material is approximately proportional to the strength of the link between the atoms in a material and to the number of links per cross section area. When stress is applied, the weakest link, i.e., the nonbonded interchain interaction, reforms much easily than the strong covalent bonds along the individual chains. Thus, the networks of nonbonded interchain interaction play a crucial role in determining the magnitude of the modulus of the polymer resin.

The results of various mechanical properties of cured NECOI at $330^{\circ}C$ and its composite with varying CCC of PAN, which is used as laminate on carbon fiber, is given in Table V. It can be inferred from the table that incorporation of different concentration of PAN in PMR matrix has significantly affected the tensile properties.

PMR+PAN as a matrix with different concentration of carbon fiber, cured at $330^{\circ}C$, shows the increase in tensile strength (Table V). Tensile strength is found to be greater than the neat PMR. This shows the influence of adhesive nature of PAN fiber and crosslinking within the gap of carbon fiber to strengthen the composite. Maximum tensile strength is obtained for specimen with $10^{-2}\%$ CCC of PAN in PMR during the formation of matrix for

TABLE V
Mechanical Properties of Pure Carbon Fiber Composite, Laminate with Pure PMR and with Varying PAN in Different Critical Crosslinking Concentration in NECOAA Matrix at $330^{\circ}C$ Cured Temperature

S. no.	Sample designation of composite	Mechanical Properties				
		Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)	Flexural strength (MPa)	Flexural modulus (GPa)
1.	Carbon fiber	391	73.5	1.71	487.6	34.12
2.	CF + Pure PMR	420.5	74.9	2.9	583.1	37.34
3.	(CF + PMR + PAN) 10^{-4}	454.5	75.4	3.1	598	38.34
4.	(CF + PMR + PAN) 10^{-3}	513.2	78.7	3.3	640	39.34
5.	(CF + PMR + PAN) 10^{-2}	535	81.3	4.1	790	42.31
6.	(CF + PMR + PAN) 10^{-1}	503	77.6	3.8	660	40.79

CF, Carbon fiber.

laminate on carbon fiber. Thus nearly twice the increase in tensile strength indicates the increase in over all mechanical strength.

CONCLUSIONS

When PAN is incorporated within the matrix of PMR resin in ultra low concentration ($10^{-2}\%$ CCC), and cured at 330°C , it gets cyclised and forms ladder structure, and an emanation of fiber is observed, which completely changes the properties of PMR resin as a whole into a new material. The formation of new resin material (PMR+PAN) shows synergistic improvement in hydraulic and chemical stability with temperature resistivity as well as improves the mechanical properties. Laminate of PMR+PAN resin on carbon fiber as a matrix to form reinforced carbon composite attributes to the enhancement of mechanical performance. These newly developed polymeric materials in form of resin and composite are assigning to be used in modern technologies like aerospace and marine system.

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