

Thermal and Mechanical Properties of Hybrid Carbon/Oxidized Polyacrylonitrile Fibers- Epoxy Composites

Hossein Ebrahimnezhad-Khaljiri, Reza Eslami-Farsani*

Faculty of Materials Science and Engineering, K. N. Toosi University of Technology, Tehran, Iran

* Corresponding author: eslami@kntu.ac.ir

Abstract

Nowadays, hybrid composites are one of the important materials in industry due to their special properties. In this research, hybrid oxidized polyacrylonitrile (PAN) and carbon fibers reinforcement were used in epoxy matrix. The hybrid composites were fabricated using the hand lay-up technique by placing the reinforcements in different layering sequences. Thermal and mechanical properties of these hybrid composites were investigated by thermal analysis, horizontal burning, tensile and bending tests. The tensile test results indicated that increasing oxidized polyacrylonitrile fibers (OPFs) to carbon fibers ratio decreased tensile strength and elastic modulus, but increased failure strain. Hybrid oxidized PAN and carbon fibers reinforcement in composites led to decreasing flexural stress and modulus, and increasing flame retardancy. Thermal analysis results also showed that the maximum rate of mass loss in all composites was 370.6°C. It was also found that the maximum and minimum amounts of char residue at 900°C were related to the composites with four layers of carbon and OPFs, respectively.

Keywords: Hybrid composite, Oxidized polyacrylonitrile fibers, Carbon fibers, Thermal analysis, Mechanical properties

1- Introduction

Polymer matrix composites have gained substantial interest over the last years, mainly due to their very high strength to weight and stiffness to weight ratios [1]. For this reason, these composites are used in industries such as aerospace, automotive, and marine industries [2, 3]. Epoxy resins are important thermosetting materials that have been widely used as advanced composite materials for their outstanding properties, such as good mechanical properties, chemical resistance, excellent electric insulating property and low manufacturing cost [4]. Among various types of reinforcement, carbon fibers have received much attention for their potential applications. The carbon fibers are very strong, stiff and lightweight [5]. Although carbon fibers-reinforced composites possess excellent overall mechanical properties, they have relatively low compressive-to-tensile strength ratio, which is a disadvantage for their use as structural members subjected to compressive and/or flexural loading [6].

The oxidized polyacrylonitrile fibers (OPFs) obtained from thermal stabilization of PAN (Polyacrylonitrile) fibers with $[C_3H_3N]_n$ chemical structure are used as precursors materials for the production of carbon fibers [7]. The commercial name of OPF is PANOX, which was used for the first time by R. K. Carbon fiber Company [8]. Researches addressing the chemical composition of PAN fibers have shown that this fiber consists of 85 wt.% acrylonitrile and 15 wt.% comonomers like IT and MA [9, 10].

Stabilization is the most complicated and time-consuming process [11-13]. In a typical process, PAN fibers are placed in an open furnace and stabilized for 1-2 h in a temperature range from 180 to 300°C. During the process, a series of gas-solid phase chemical reactions may occur; these reactions primarily include cyclization, dehydrogenation and oxidation. Firstly, the cyclization is the conversion of nitrile groups ($-C\equiv N$) into conjugated carbon-

nitrogen double bonds ($-C=N-$); secondly, the dehydrogenation results in the formation of carbon-carbon double bond and conjugated structures in PAN macromolecules; thirdly, the oxidation introduces oxygen-containing groups such as carbonyl groups ($-C=O$). These three types of reactions can lead to ladder-like molecular structures, making the oxidized PAN fibers heat resistant and infusible [9, 13, 14].

Further researches on the mechanical properties of PAN fibers have shown that increasing the time of thermal stabilization decreases tensile strength and elongation, but elastic modulus is increased at beginning and then decreased. This decrease in the mechanical properties is a result of nitrile to nitro group transformation during thermal stabilization. Over oxidation in the temperature range during thermal stabilization is another reason for the decrease in mechanical properties [15]. The results of researches have shown that by increasing the heating rate up to $2^{\circ}\text{C}/\text{min}$, strength is rapidly increased, and then this increase is gradual [16].

In a hybrid composite, two or more types of fibers are used to reinforce a common matrix. Hybrid composites are composed of more than one type of reinforcement because properties are optimized. Hybrid composites can be classified into interply or laminated hybrids, intraply or tow-by-tow hybrids, intimately mixed hybrids, and other types of mixtures [17]. Carbon fibers are hybridized in composites by glass, Kevlar, basalt and other types of fibers [3, 17-19]. The hybridization of carbon fibers and OPF in composites has not been performed yet. For this reason, the purpose of this research was to study thermal and mechanical properties of hybrid carbon fibers-OPF reinforced epoxy composite.

2- Experimental

2-1- Materials

The epoxy resin used for this study was the blending of epoxy Bisphenol F resin (ML-506)

and polyamine hardener (HA-11) (Mokarrar engineering materials, Iran). The resin to hardener ratio was kept to be 100:15 part by weight. The carbon fibers fabrics (G. Angeloni, Italy) in the form of twill 2×2 (200 g/m²) and OPF with 1.16 dtex linear density (Courtaulds, UK) were used in this study.

2-2- Composite Preparation

The hybrid composites were made in the form of 4 layer composites with different layering of carbon fibers and OPF reinforcements in the epoxy matrix (Fig. 1), using hand lay-up method. The coding system of these composites has been listed in Table 1. The resin to reinforcement ratio, due to high absorption resin by OPF, was selected to be 60:40 wt.%. The curing time for these composites was 24 h at the ambient temperature.

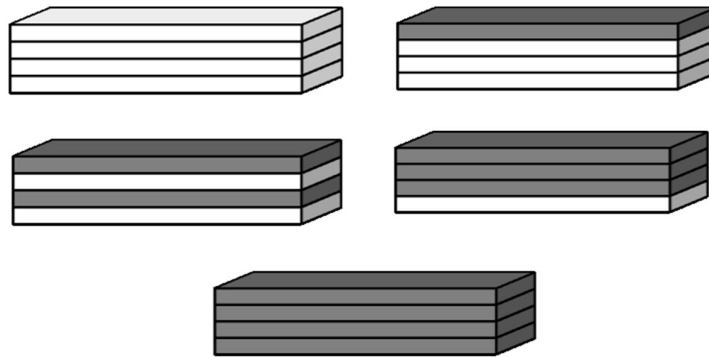


Figure 1. Different plies of composites, Black layer: OPF, White layer: Carbon fibers.

Table 1. Composites code.

Code of composite	Number of plies	OPF/total reinforcement ratio (%)
0P-4C	4	0
1P-3C	3	48
2P-2C	2	76
3P-1C	1	89
4P-0C	0	100

P: OPF and C= Carbon fibers fabric

2-3- Instruments and Characterization

- Thermal Analysis

Thermal decomposition of hybrid carbon fiber-OPF reinforced epoxy composites was investigated using thermogravimetric analyzer (TG, NETZSCH TG 209 F1 Iris, Germany). TG tests were performed at the heating rate of 20°C/min and in the temperature range of 30-900°C, under nitrogen gas. The sample mass was ~10 mg.

- Flammability Testing

The UL-94 horizontal burning test was performed according to ASTM D 635 with these dimensions: 125 × 12.5 × 2.8 mm³ (length × width × thickness) [20]. At least three samples were examined and the average value was reported.

- Tensile test

The tensile test of composites was performed by Hounsfield H25KS tester to load up 25 kN and cross head 2 mm/min. The samples were cut and polished with the dimension of 250×20 mm², according to ASTM D3039-00 [21]. The gauge length was set 100 mm and abrasive papers P80 were used to its ends for gripping and ensuring failure within the gauge

region. At least five samples were examined and the average value was reported.

- Flexural test

The flexural test of the composites was performed by Hounsfield H25KS tester with 500N load cell. The flexural performance was measured in three point bending mode, according to ASTM D790-00 method. The samples with the dimension of 100×20 mm² were cut and polished. The support span length and cross head speed were set to be 80 mm and 4.3 mm/min, respectively, according to ASTM D790 [22]. At least five samples for each composite were tested and the average value was reported.

3- Results and Discussion

3-1- Thermal Properties of Composites

Figs. 2 and 3 indicate TG and derivative thermogravimetric (DTG) curves of hybrid OPF-carbon fibers reinforced composites. Table 2 summarizes some data obtained from TG and DTG curves that included the decomposition temperature recorded at 5% mass loss ($T_{5\%}$), the onset decomposition temperature (T_0), the temperature of the maximum rate of mass loss (T_{max}) and char residue at 900°C. From Table 2, it could be seen that increasing OPF to carbon fibers ratio decreased $T_{5\%}$. 0P-4C and 4P-0C composites with the temperature of 338°C and 255.7°C had the maximum and minimum decomposition temperatures recorded at 5% mass loss, respectively. Onset decomposition temperatures of hybrid composites showed the similar behavior of $T_{5\%}$, except in 3P-1C composite. Therefore, 0P-4C and 4P-0C composites had the maximum and minimum T_0 , respectively.

From Fig. 3, it could be seen that there were two stages of mass loss. The first stage was a slow mass loss at the range of 150 - 250°C and second one was rapid mass loss at the range of 300-500°C. The first stage mass was loss mainly caused by pendant chain of epoxy, while the

second stage mass loss resulted from the decomposition of the main chain in the epoxy resin [23], and carbonization of OPF at high temperature in nitrogen atmosphere. The results of DTG curves showed that the temperature of the maximum rate of mass loss of all composites was 370.6°C. Further researches showed that OPFs were precursor materials for the production of carbon fibers [24]. When OPFs are inside furnace at high temperature in nitrogen atmosphere, carbonization reactions occur and OPFs are transformed in to carbon fibers [7, 24]. For this reason, OPF has a behavior similar to that carbon fibers in TG analyzer at high temperature and under nitrogen atmosphere.

Fig. 4 illustrates char residue-percent of OPF per total reinforcement curves. From Fig. 4, it could be seen that 0P-4C and 4P-0C composites with 53.36% and 25.95% char residue had the maximum and minimum char residue, respectively. 1P-3C and 3P-1C composites had the same char residue, but 2P-2C composite showed lower char residue at 900°C due to the difference in the rate of mass loss and heat transfer, between OPF and carbon fibers plies.

Table 2. Thermal properties of hybrid composites recorded from TG and DTG.

Code of composite	T _{max} (°C)	T _{5%} (°C)	T _o (°C)	Char residue at 900°C (%)
0P-4C	370.60	338.00	320.00	53.36
1P-3C	370.60	300.60	300.63	35.01
2P-2C	370.60	305.00	300.63	32.09
3P-1C	370.60	290.65	280.65	35.60
4P-0C	370.60	255.70	290.65	25.95

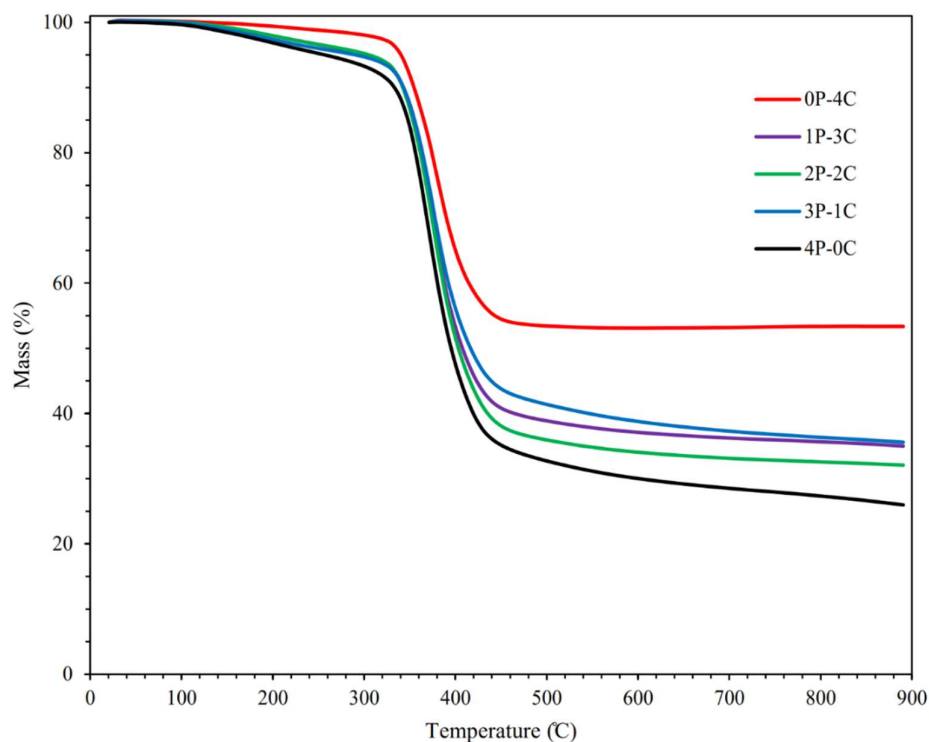


Figure 2. TG curves of hybrid carbon fibers- OPF/ epoxy composites.

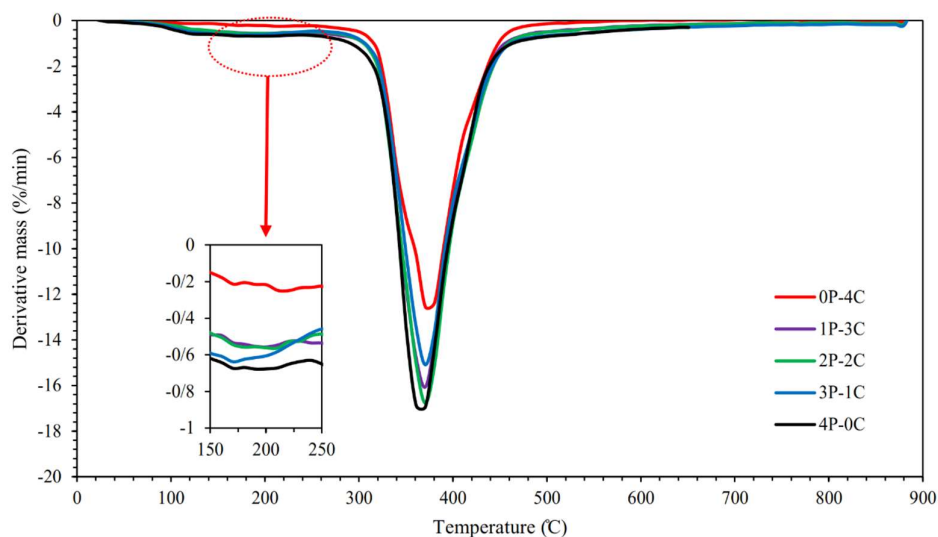


Figure 3. DTG curves of hybrid carbon fibers-OPF/ epoxy composites.

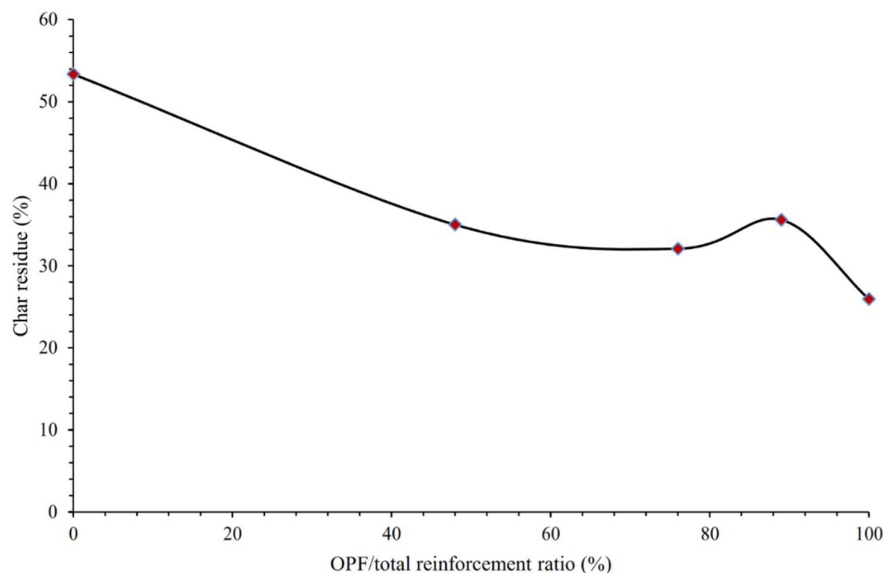


Figure 4. Chare residue- OPF/total reinforcement curve.

3-2- Flammability Testing of Composites

The results of UL-94 horizontal burning technique have been listed in Table 3. Fig. 5 demonstrates the burning rate of hybrid composites. From Fig. 5, it could be seen that 0P-4C and 4P-0C composites with 26.78 and 8.13 mm/min rate of burning had the maximum and minimum rates of burning, respectively. Increasing OPF to carbon fibers ratio decreased the burning rate of hybrid composites, thereby increasing the flame retardancy of hybrid composites due to the chemical structure of OPF Fig. 6 [7]. From Fig. 6, it could be seen that OPF had 40% oxidized structure; also, for achieving burning reactions, there had to be broken chains of OPF or carbon fibers. Chain scission of OPF needed a high level of energy than the chain scission of carbon fibers. For this reason, OPF was more flame retardant than carbon fibers.

Table 3. UL-94 horizontal burning of composites.

Code of composite	0P-4C	1P-3C	2P-2C	3P-1C	4P-0C
Rate of burning (mm/min)	26.78±0.60	15.54±0.45	11.61±0.35	10.23±0.25	8.13±0.30

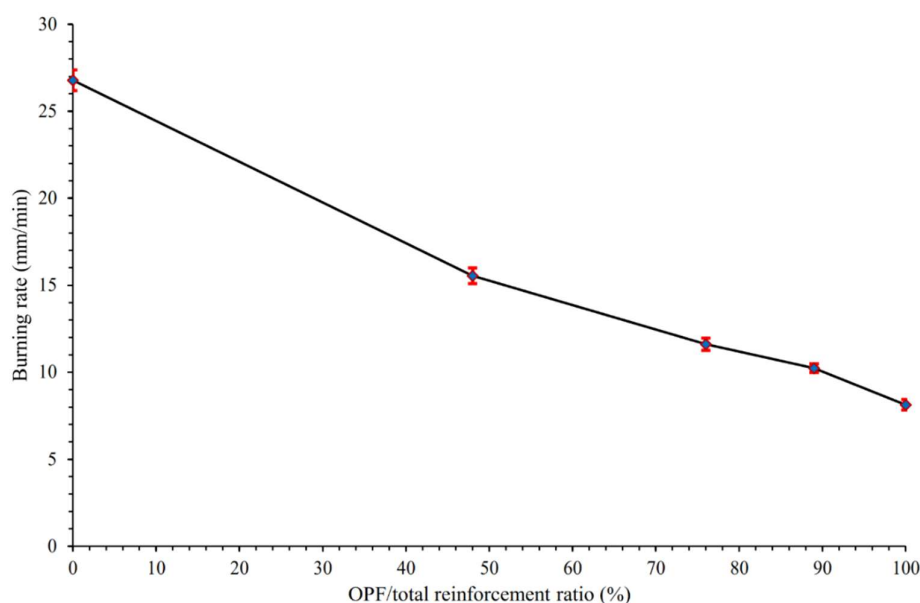


Figure 5. Burning rate of hybrid carbon fibers-OPF/ epoxy composites.

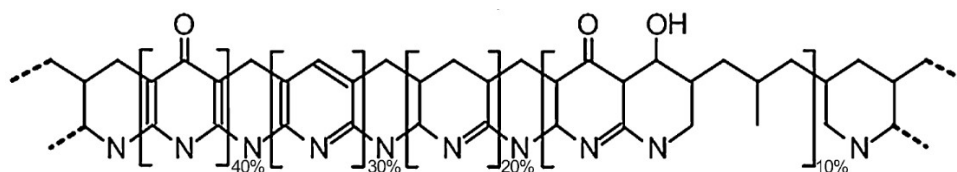


Figure 6. Chemical structure of stabilized PAN [7].

3-3- Tensile Test of Composites

The data obtained from tensile test for hybrid carbon fibers-OPF reinforced epoxy composites with different weight percentages of OPF containing tensile strength, elastic modulus and failure strain has been listed in Table 4 and Figs. 7-9, respectively. This data was calculated according to standard test method ASTM D3909 [21].

From Fig. 7, it could be seen that 0P-4C and 4P-0C composites with 566.40 and 61.07 MPa tensile strength had the maximum and minimum tensile strength, respectively. Increasing OPF to carbon fibers ratio in hybrid composites decreased tensile strength due to the low tensile strength of OPF. During thermal stabilization of PAN, tensile strength was decreased due to the change in the structure [10]. For this reason, OPF had low tensile strength. The elastic modulus of hybrid composites showed a similar behavior. From Fig. 8, it could be observed that 0P-4C and 4P-0C composites with 42.45 and 4.87 GPa elastic modulus had the maximum and minimum elastic modulus, respectively. Increasing OPF to carbon fibers ratio in hybrid composites decreased elastic modulus due to the low elastic modulus of OPF.

From Fig. 9, it could be understood that 0P-4C composite had 1.3% failure strain. Increasing the weight percent of OPF to carbon fibers ratio up to 48% decreased failure strain to more than 48 wt.%; on the other hand, increasing weight percent of OPF to carbon fibers ratio enhanced the failure strain. Also, adding OPF to carbon fibers reinforced composites increased the failure strain. But this initial failure strength decrease was due to the mismatch between OPF and carbon fibers. The composite reinforced by the four layers OPF with 1.68% failure strain had the maximum failure strain.

Table 4. Results of tensile test.

Code of composite	Tensile strength (MPa)	Elastic modulus (GPa)	Failure strain (%)
0P-4C	566.4 ± 15.80	42.45 ± 0.48	1.30 ± 0.03
1P-3C	261.38 ± 12.30	25.00 ± 0.60	1.05 ± 0.01
2P-2C	154.54 ± 8.09	12.69 ± 0.40	1.19 ± 0.04
3P-1C	103.11 ± 2.70	8.86 ± 0.20	1.22 ± 0.05
4P-0C	61.07 ± 6.73	4.87 ± 0.06	1.68 ± 0.04

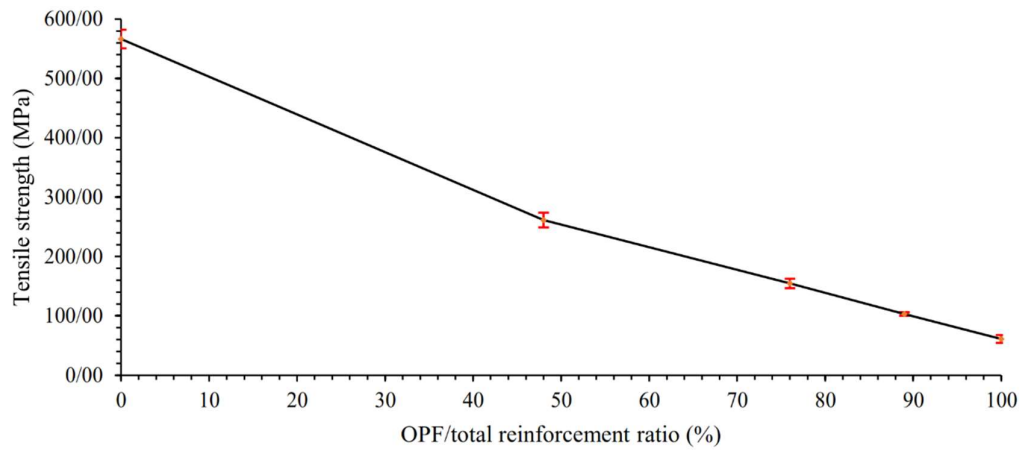


Figure 7. Tensile strength of hybrid carbon fibers-OPF/ epoxy composites.

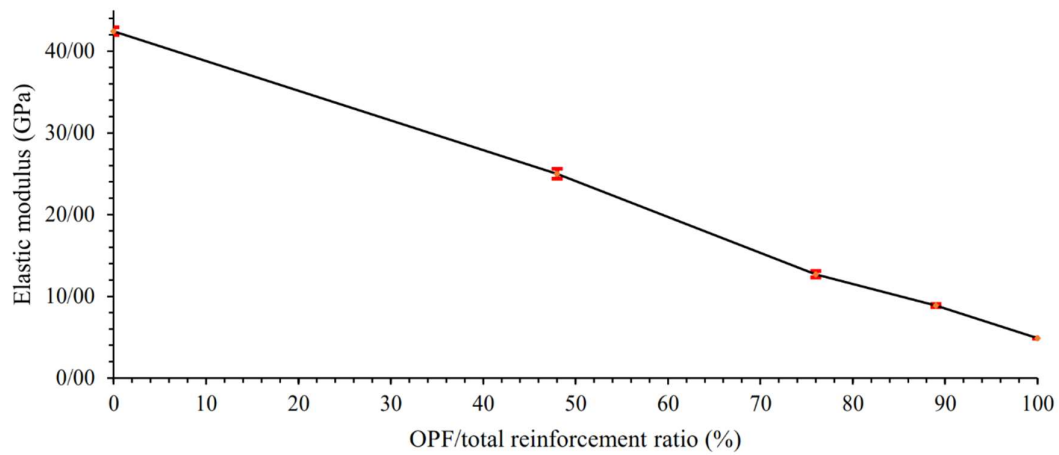


Figure 8. Elastic modulus of hybrid carbon fibers-OPF/ epoxy composites.

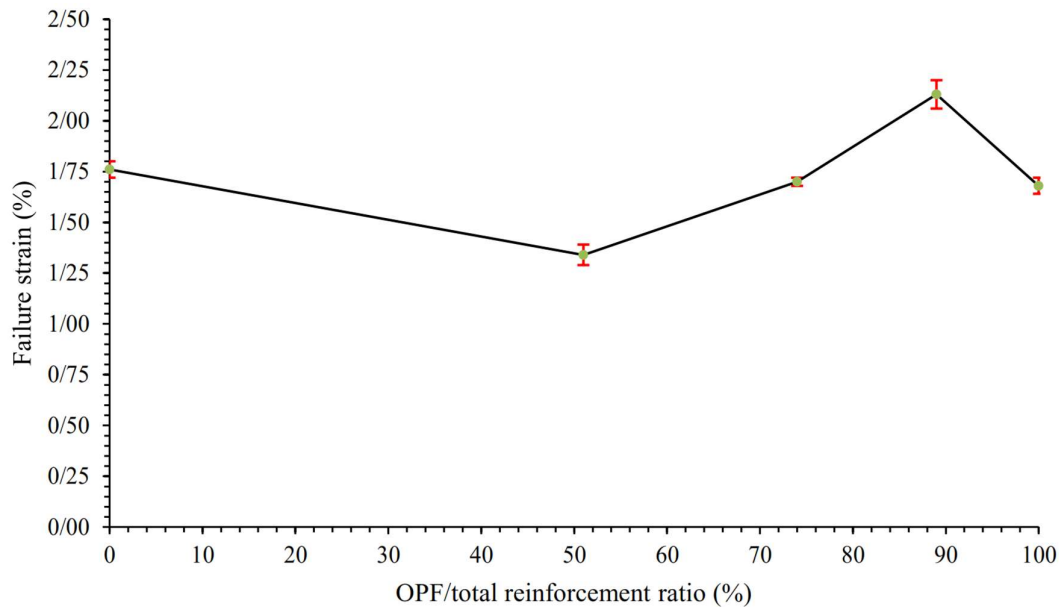


Figure 9. Failure strain of hybrid carbon fibers-OPF/ epoxy composites.

3-4- Bending Test of Composites

The data obtained from the bending test for hybrid carbon fibers-OPF reinforced epoxy composites with different weight percentages of OPF containing flexural stress and flexural modulus has been listed in Table 5, and Figs. 10 and 11, respectively. This data was obtained according to standard test method ASTM D790 [22].

From Fig. 10, it could be seen that 0P-4C and 4P-0C composites with 447.59 and 107.97 MPa flexural stress had the maximum and minimum flexural stress, respectively. Increasing the weight percent of OPF to carbon fibers ratio enhanced the flexural stress. From Fig. 11, it could be observed that 0P-4C and 4P-0C composites with 41.28 and 4.78 GPa flexural modulus had the maximum and minimum flexural modulus, respectively. Increasing OPF to carbon fibers ratio in hybrid composites decreased flexural modulus due to the low flexural modulus of OPF.

Table 5. Results of flexural test.

Code of composite	Flexural stress (MPa)	Flexural modulus (GPa)
0P-4C	447.59 ± 12.83	41.28 ± 0.80
1P-3C	357.97 ± 8.31	23.61 ± 0.43
2P-2C	279.36 ± 10.25	12.01 ± 0.75
3P-1C	210.33 ± 7.42	8.52 ± 0.50
4P-0C	107.97 ± 5.59	4.78 ± 0.33

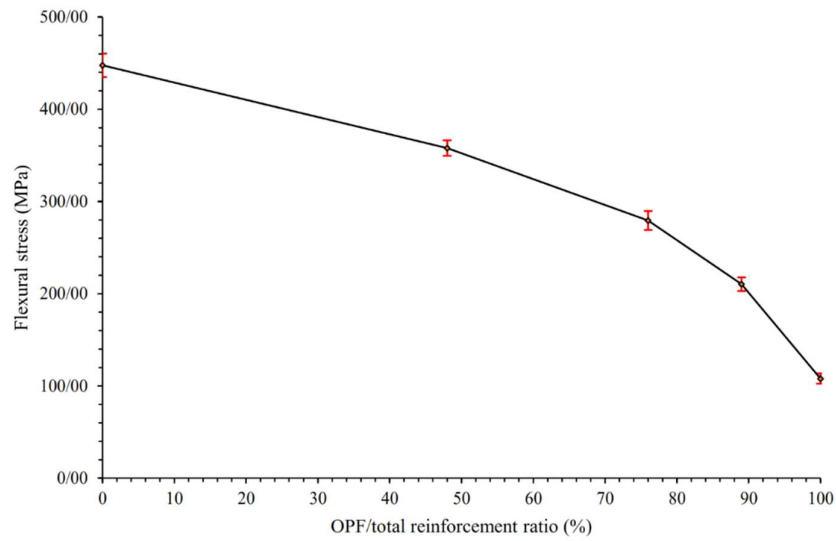


Figure 10. Flexural stress of hybrid carbon fibers-OPF/ epoxy composites

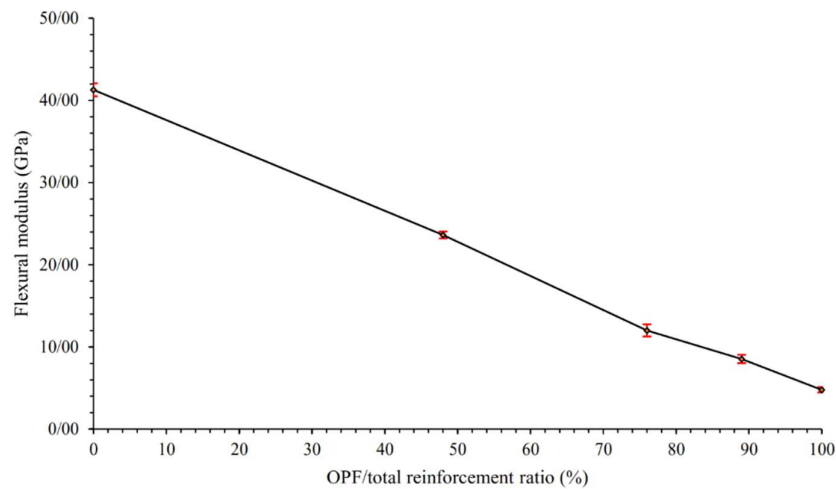


Figure 11. Flexural modulus of hybrid carbon fibers-OPF/ epoxy composites.

4- Conclusions

In this research, oxidized polyacrylonitrile and carbon fibers were hybridized into epoxy matrix with different layering sequences. Then, mechanical and thermal properties of these composites were studied. The following conclusions could be drawn:

- 1) The results of TG and DTG curves demonstrated that oxidized polyacrylonitrile and carbon fibers showed a similar behaviour at high temperatures in nitrogen atmosphere, but they had different rates of mass loss and heat transfer.
- 2) The results of flammability test indicated that flame retardancy of hybrid composites was increased with the enhancement of oxidized polyacrylonitrile fibers to carbon fibers ratio.
- 3) The results of tensile and bending tests showed that by increasing the ratio of oxidized polyacrylonitrile fibers to carbon fibers, tensile strength, elastic modulus, flexural stress and modulus were decreased, but failure strain was increased.

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