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The Effect of Hybridization on Thermal and Mechanical Properties of Glass/Oxidized PAN Fibers-Polymer Composites

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Abstract: Fibers hybridization is one of the most effective ways to facilitate the use of the new fibers as reinforcement in composite materials. In this study, oxidized polyacrylonitrile fibers (OPFs) and glass fibers were hybridized in a polymer matrix through hand lay-up method by arranging the fibers in different layering sequences. The hybridization effects of fibers on thermal and mechanical properties of the polymer matrix composites were investigated by thermal analysis, horizontal burning, tensile and flexural testes. It was found that by increasing the OPFs to glass fibers ratio, tensile strength, elastic and flexural modulus and flexural stress were decreased, whereas failure strain followed a different trend. Also, hybridization of OPFs and glass fibers in composites led to decreasing the burning rate and consequently, increasing fire retardancy. The obtained thermogravimetric analysis results also demonstrated that maximum and minimum amounts of char residue at 900 °C were related to the composites reinforced with four layers of glass fibers and OPFs, respectively. Based on the results of derivative thermogravimetric (DTG), by increasing the OPFs to glass fibers ratio, DTG curves were shifted to higher temperatures.

Keywords: Hybrid composite, Oxidized polyacrylonitrile fibers, Glass fibers, Thermal properties, Mechanical properties

Introduction

During the two last decades, composite materials have been successfully used in industry and engineering due to their excellent properties [1-5]. Among various types of fibers, glass fibers are preferred due to their high modulus, high toughness and low density. Epoxy resin, as compared with other resins, is favourable for usage in composites as matrix. This is because of suitable mechanical and physico-chemical properties of epoxy resin [6]. For achieving other suitable properties in glass fibers reinforced epoxy composites, such as resistance in elevated temperatures, compatibility with the environment, resistance in oxidized atmosphere and lower economic costs, researches have focused on the development of suitable conditions for using other fibers in composite industries [7,8].

Fibers hybridization is one of the most simple and effective ways which can facilitate the use of the new fibers as reinforcement. Also, other properties improved in the glass fibers reinforced composites have rarely been obtained with the glass fibers. The glass fibers can be hybridized with other fibers such as carbon, Kevlar and basalt by three different configurations including interlayer (layer-by-layer), intralayer (yarn-by-yarn), and intrayarn (fiber-by-fiber) [9].

In the interlayer configuration, layers of different fibers are stacked onto each other. This configuration is the most common type, due to its easier fabrication [10]. In the intralayer configuration, the layers include two or more constituent types of fibers which are alternatively arranged within the layers. These two types of fibres can also be mixed or commingled on the fibres level, resulting in an intrayarn hybrid which has the best degree of distribution and the most effects on the hybrid composites, as compared to other configurations [11].

Oxidized polyacrylonitrile fibers (OPFs) have special properties such as high thermal resistance, insolubility, high melting point, high electrical resistance, and compatibility with environment [12,13]. But the OPFs have weak tensile strength, due to the presence of weak cross links in their molecular structures [14]. The OPFs are obtained from thermal stabilization of polyacrylonitrile (PAN) fibers including 85 wt. % acrylonitrile and 15 wt. % comonomers [15]. The comonomers are added to improve the OPFs properties. They can be classified in two categories: neutral comonomers like methyl acrylate (MA), vinyl acetate (VA), or methyl methacrylate (MMA), and ionic-acidic comonomers such as sodium methallyl sulfonate (SMS), sodium 2-methyl-2-acrylamidopropanesulfonate (SAMPS), itaconic acid (IA) and sodium p-styrenesulfonate (SSS). Also, some comonomers like IA facilitate the OPFs fabrication [16,17].

The thermal stabilization is the most complicated and time-consuming process [18,19]. During this process, the PAN fibers are heated at the temperature range of 180-280 °C for about 1 h. The stabilization of PAN fibers is conducted in air because it has better mechanical properties, as compared with the stabilized PAN in the inert atmosphere [20]. During the thermal stabilization, exothermic reactions including cyclization, dehydrogenization and oxidation occur [21].

Many studies have focused on the hybridization of glass fibers with other high performance fibers such as carbon, Kevlar and basalt fibers [22-25]. To the best our knowledge, the hybridization of glass fibers and OPFs in the composites has not been reported yet. Therefore, the aim of this study

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was to investigate the thermal and mechanical properties of hybrid glass fibers-OPFs/epoxy composites fabricated through hand lay-up method by arranging the fibers in different layering sequences.

Experimental

Materials

The resin used for this study was some epoxy resin that was obtained by blending 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 glass fibers (Camelyaf, Turkey) in the form of the woven roving (200 g/m^2) and the OPFs with 1.16 dtex linear density (Courtaulds, UK) were used in this study.

Composite Preparation

The hybrid composites were fabricated in the form of 4 layer epoxy matrix composites by using hand lay-up method and arranging the glass fibers and OPFs reinforcements in different layering sequences, as shown in Figure 1. The coding system of these composites has been listed in Table 1. The resin to reinforcement ratio, due to high absorption resin by OPFs, was selected to be 60:40 wt. %. The curing time for these composites was 24 h at the ambient temperature.

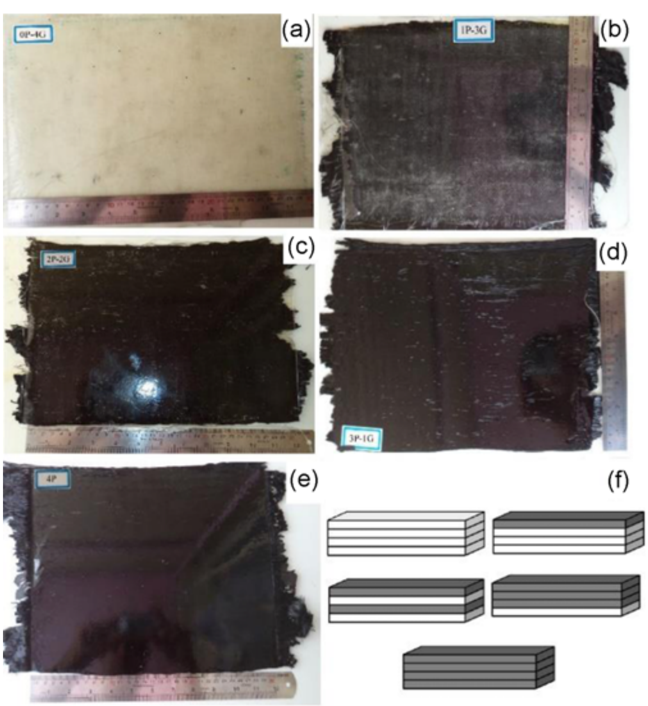

Figure 1. Fabricated hybrid composites; (a) 0P-4G, (b) 1P-3G, (c) 2P-2G, (d) 3P-1G, (e) 4P-0G, and (f) different stacking sequences (black layer: OPFs, white layer: glass fibers).

Table 1. Composites code

Code of composite	Number of layers of glass fiber	OPF/total reinforcement ratio (%)
0P-4G	4	0
1P-3G	3	51
2P-2G	2	74
3P-1G	1	89
4P-0G	0	100

P: OPFs, G: glass fibers.

Instruments and Characterization

Thermal Analysis

Thermal decomposition of hybrid glass fibers-OPFs/epoxy composites was investigated using thermogravimetric (TG) analyzer (TG, NETZSCH TG 209 F1 Iris, Germany). TG tests were performed at the heating rate of 20 ^{o}C/min and the temperature range of 30-900 ^{o}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 mm^3 (length×width×thickness) [26]. For more accuracy, 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 mm^2, according to ASTM D3039 [27]. The gauge length was set to be 100 mm and abrasive papers P80 were used up to their ends for gripping and ensuring failure within the gauge region. For more accuracy, 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 the three point bending mode, according to ASTM D790 method. The samples with the dimensions of 100×20 mm^2 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 [28]. For more accuracy, at least five samples for each composite were tested and the average value was reported.

Results and Discussion

Thermal Properties of Composites

Figure 2 and Figure 3 present the TG and derivative thermogravimetric (DTG) curves for hybrid glass fibers-OPFs/epoxy composites with different stacking sequences. Table 2 summarizes some data extracted from TG and DTG curves, including the decomposition temperature recorded at

5 % mass loss (T5%), the onset decomposition temperature (T_o), the temperature of the maximum rate of mass loss (T_{max}) and char residue.

As shown in Figure 2, all composites had similar decomposition curves. Also, the range of char residue at 900 °C was variable from 25.95 to 59.63. It should be clarified that 4P-0G and 0P-4G composites had the minimum and maximum char residues, respectively. By increasing the OPFs to glass fibers ratio, char residue was decreased in all composites, except in 2P-2G composite, in which char residue was increased. This was because of the difference in the rate of mass loss and heat transfer between OPFs and glass fibers layers. This trend revealed that the hybrid composites with a higher degree of uniformity were more thermally stable. This was also in a good agreement with other hybrid composites [29].

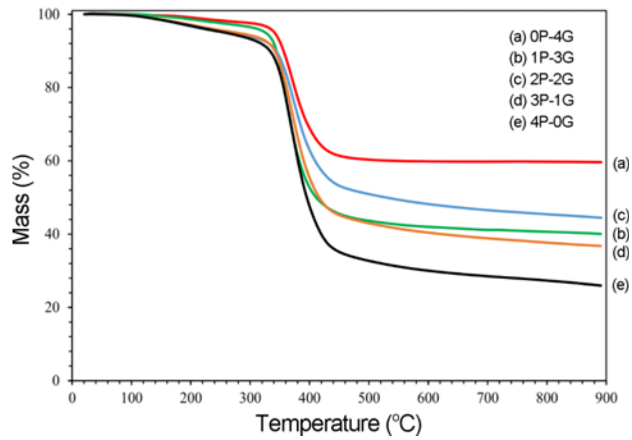

Figure 2. TG curves of hybrid glass fibers-OPFs composites.

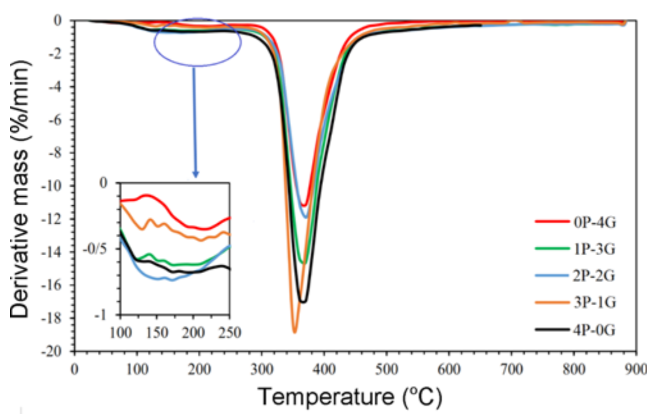

Figure 3. DTG curves of hybrid glass fibers-OPFs composites.

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-4G	371.4	341.4	331.0	59.63
1P-3G	350.9	325.0	290.4	40.04
2P-2G	371.0	261.0	291.5	44.49
3P-1G	340.5	270.0	310.5	36.70
4P-0G	370.6	255.7	290.6	25.95

The addition of OPFs into the glass fibers reinforced epoxy composite caused DTG curves to be shifted to higher temperatures. From Figure 3, it could be seen that there were two stages of mass loss: a slow mass loss at the range of 100-250 °C and a rapid mass loss at the range of 300-500 °C. The first stage mass loss was mainly caused by the pendant chain of epoxy, while the second one resulted from the decomposition of the main chain in the epoxy resin [30], and carbonization of OPFs at high temperature in nitrogen atmosphere. When OPFs were set into the furnace in the nitrogen atmosphere, they were transformed in to carbon fibers. For this reason, gases such as NH_3 and HCN could be released from inside the OPFs, slightly increasing the second mass loss [31].

Flammability Testing of Composites

The results of UL-94 horizontal burning technique have been listed in Table 3. Figure 4 shows the burning rate of hybrid composites. From Figure 4, it could be observed that 0P-4G and 4P-0G composites had the maximum and minimum rates of burning, respectively. Increasing the OPFs to glass fibers ratio decreased the burning rate of hybrid composites, thereby increasing the flame retardancy of the hybrid

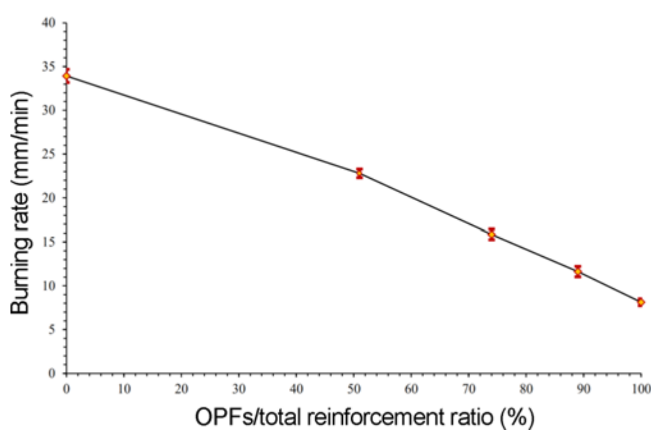

Figure 4. Burning rate of hybrid glass fibers-OPFs composites.

Table 3. UL-94 horizontal burning of composites

Code of composite	0P-4G	1P-3G	2P-2G	3P-1G	4P-0G
Rate of burning (mm/min)	33.93±0.75	22.79±0.50	15.86±0.60	11.62±0.60	8.13±0.40

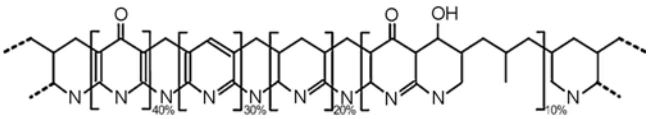

Figure 5. Chemical structure of stabilized PAN [8].

composites due to the cyclized and oxidized structure of OPFs (see in Figure 5) [14]. For the accomplishment of burning reactions, OPFs had to be reacted with oxygen. But 40 % oxidized structure reduced the trend of OPFs for achieving the reaction with oxygen. On the other hand, for the accomplishment of reaction with the the remaining 60 % structure, the chemical structure had to be broken to chains and bonds of OPFs, which needed a high level of energy [31]. For these reasons, OPFs had flame retardancy properties.

Tensile Test of Composites

The data obtained from tensile test for hybrid glass fibers-OPFs/epoxy composites containing tensile strength, elastic modulus and failure strain has been listed in Table 4 and Figures 6-8, respectively. From Figure 6, it could be seen that 0P-4G and 4P-0G composites with 215.91 and 61.07 MPa tensile strength had the maximum and minimum tensile strength, respectively. Increasing OPFs to glass fibers ratio in the hybrid composites decreased tensile strength due to the low tensile strength of OPFs. During thermal stabilization of PAN, tensile strength was decreased due to the change in the structure [14]. For this reason, OPFs had low tensile strength. The elastic modulus of hybrid composites showed a similar tensile strength behaviour. From Figure 7, it could be observed that the 0P-4G and 4P-0G composites with 12.80 and 4.87 GPa elastic modulus had the maximum and minimum elastic modulus, respectively.

The OPFs and glass fibers had different coefficients of linear expansion and epoxy resin binds these fibers together during curing process, resulting in the creation of tensile and pressure stresses as residual stress in the hybrid composites. It may be assumed that the pressure stresses are created on the fibers with lower tensile strength (OPFs), whereas the tensile stresses are created on the fibers with higher tensile strength (glass fibers). During tensile test, the pressure stresses can reduce the effects of tensile stresses from tensile test; on the contrary, tensile stresses can increase the effects of tensile stresses from tensile test [11]. The main conclusion drawn from the above discussions is that the apparent tensile strength created is higher than that of OPFs and lower than that of glass fibers. For this reason, hybridization of OPFs and glass fibers proves the possibility of using OPFs in the composite industries.

Based on Figure 8, it could be understood that 1P-3G hybrid composite had lower failure strain, as compared to 0P-4G composite, due to the effect of the higher degree of mismatch between glass fibers and OPFs. It could also be inferred realized that 3P-1G composites had the maximum failure strain, as compared with other composites. During the curing process, in addition to the creation of apparent tensile strength, apparent failure strain was also created,

Table 4. Results of tensile test

Code of composite	Tensile strength (MPa)	Elastic modulus (GPa)	Failure strain (%)
0P-4G	215.91±9.65	12.80±0.30	1.76±0.04
1P-3G	120.90±10.73	7.96±0.50	1.34±0.05
2P-2G	96.36±12.62	6.70±0.25	1.70±0.02
3P-1G	81.75±7.65	5.30±0.15	2.13±0.07
4P-0G	61.07±6.73	4.87±0.06	1.68±0.04

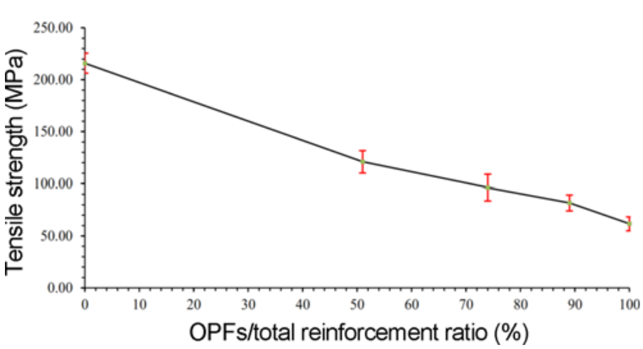

Figure 6. Tensile strength of hybrid glass fibers-OPFs composites.

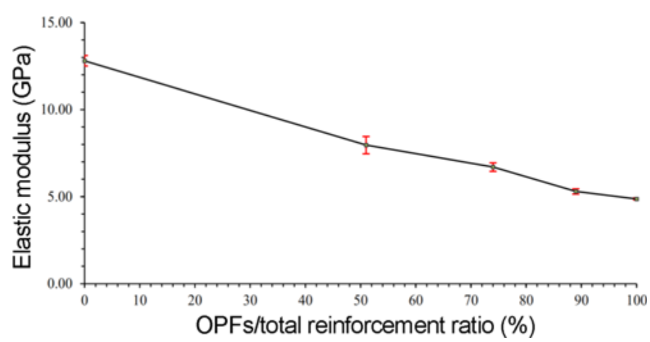

Figure 7. Elastic modulus of hybrid glass fibers-OPFs composites.

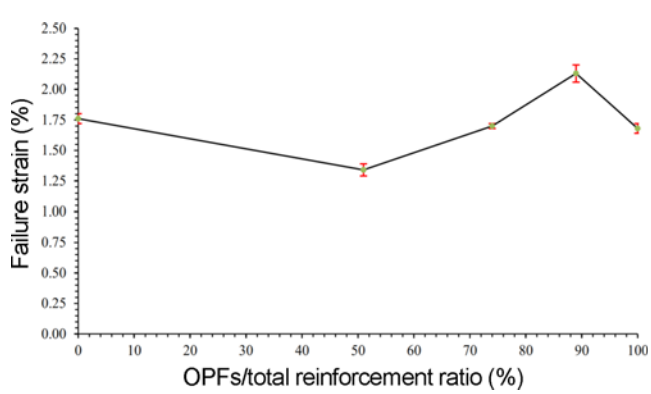

Figure 8. Failure strain of hybrid glass fibers-OPFs composites.

thereby increasing the failure strain of fibers with lower failure strain; on the contrary, it reduced the failure strain of fibers with higher failure strain [11]. This apparent failure strain could be related to the percentage of hybridized fibers in the hybrid composites. The other important factor is the uniformity of fibers in the hybrid composites. The influence of apparent failure strain and the uniformity of fibers led to the higher failure strain 3P-1G composite, as compared to other composites.

Flexural Test of Composites

The data obtained from flexural test for hybrid glass fibers-OPFs/epoxy composites with different stacking sequences of OPFs and glass fibers containing flexural stress and flexural modulus has been reported in Table 5 and Figure 9 and 10, respectively.

From Figure 9, it could be seen that 0P-4G composite with 250.93 MPa flexural stress and 4P-0G composite with 107.97 MPa flexural stress had the maximum and minimum flexural stress, respectively. Increasing the weight percentage of OPFs to glass fibers ratio enhanced flexural stress. From Figure 10, it could be observed that 0P-4G and 4P-0G composites with 13.04 and 4.78 GPa flexural modulus had the maximum and minimum flexural modulus, respectively.

Based on the results, it could be argued that 2P-2G composite, due to its higher degree of uniformity, had higher flexural stress, as compared with the other hybrid composites [10,11], whereas 1P-3G had the higher flexural stress, as compared with the other two hybrid composites. OPFs have

Table 5. Results of flexural test

Code of composite	Flexural stress (MPa)	Flexural modulus (GPa)
0P-4G	250.93±10.10	13.04±0.63
1P-3G	210.74±4.32	9.65±0.52
2P-2G	167.30±6.21	7.03±0.50
3P-1G	153.08±4.21	6.19±0.45
4P-0G	107.97±5.59	4.78±0.33

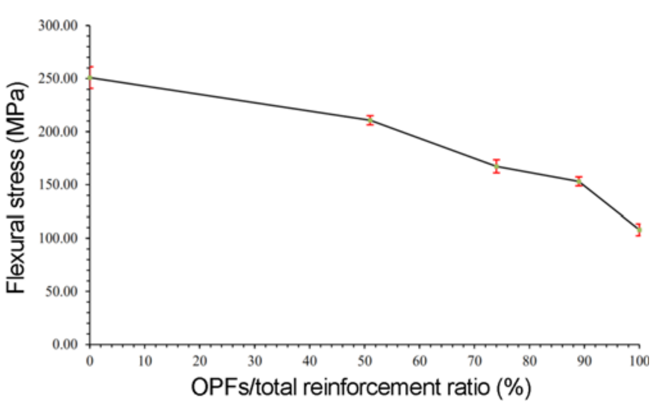

Figure 9. Flexural stress of hybrid glass fibers-OPFs composites.

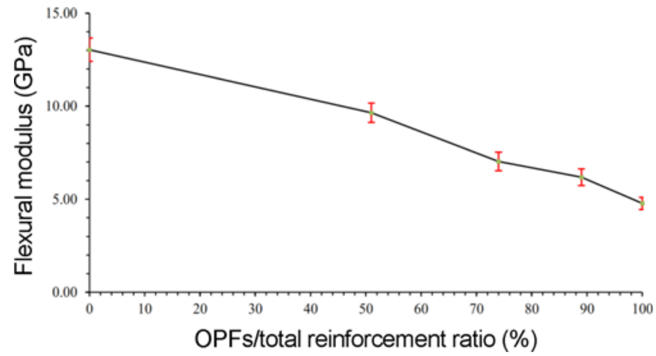

Figure 10. Flexural modulus of hybrid glass fibers-OPFs composites.

polymer chain structures which increase the flexural stress of these fibers. During flexural test, on the upper and lower layers of composites, pressure and tensile stresses were applied, respectively. According to the related research, glass fibers in the hybrid composites are the failed area under the tensile stresses [11]. For this reason, probably, the created tensile stresses on the glass fibers caused the failure of 2P-2G sample and consequently, reduced the flexural stress of this composite.

Conclusion

In this study, the oxidized polyacrylonitrile fibers (OPFs) and glass fibers were hybridized in epoxy matrix through hand lay-up method by arranging the fibers in different layering sequences. Then, the effects of fibers hybridization on thermal and mechanical behavior of composites were investigated. The following conclusions could be drawn:

1. Adding OPFs into glass fibers-epoxy composites caused DTG curves to be shifted to higher temperatures. Also, by increasing the degree of uniformity, char residue of composites at high temperatures was enhanced.
2. The results of horizontal burning showed that by increasing OPFs to glass fibers ratio, flame retardancy of composites was increased.
3. Based on the results of tensile and flexural tests, by increasing OPFs to glass fibers ratio, tensile strength, flexural stress, elastic and flexural modulus were decreased, whereas failure strain of composites was improved.
4. According to the obtained results, composites reinforced with high degree distribution of OPFs and glass fibers could be recommended for usage in industries needing simultaneous mechanical properties and flame retardancy, such as some parts around motor in automotive, aircraft and construction industries.

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