PREPARATION AND INTERFACIAL PRPPERTY OF GRAPHENE OXIDE/BPEI/CARBON FIBER HIERARCHICAL REINFORCEMENT

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Keywords: Polymer based composites，Interfacial design of composite，Hierarchical Reinforcement，Carbon fiber

ABSTRACT

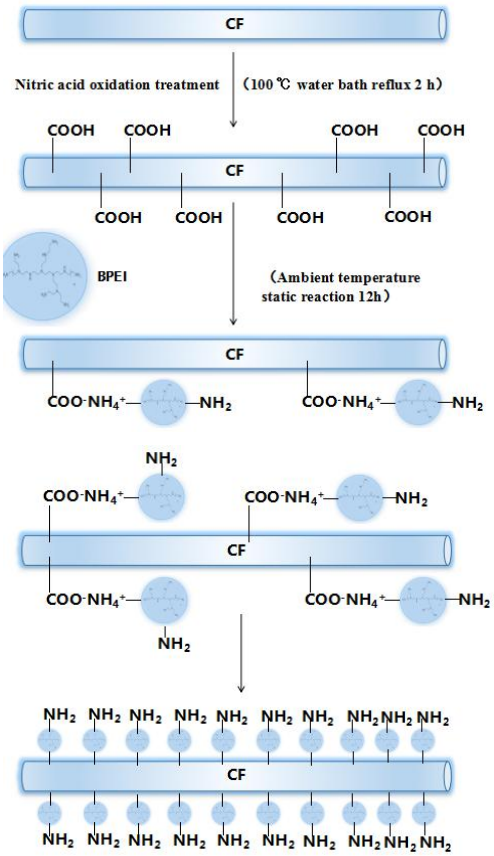
Prepared branched polyethylenimine(BPEI) grafted carbon fiber hierarchical reinforcement through electrostatic interaction; verified the branched polyethyleneimine and carbon fiber connected by chemical bond by XPS; the surface energy test suggested that the introduction of branched polyethyleneimine made the carbon fiber hierarchical reinforcement's surface energy increased 90% and improved the adhesive properties of carbon fiber and polymer matrix; the results of XPS analysis, trend of changes in the surface energy and micro droplet bonding results showed that when branched polyethyleneimine solution concentration is 0.1% wt, made the largest contribution on the interface strength, the interfacial shear strength enhanced 46.34% compared to raw carbon fiber .

With branched polyethyleneimine as the medium, the graphene oxide was grafted onto the surface of carbon fiber, the mechanical interlock of carbon fiber reinforcement and polymer matrix was strengthened, and it improved the surface energy of carbon fiber, and then improved the interface strength of the composite. The surface chemical state of carbon fiber reinforcement characterized by XPS confirmed that the branched polyethyleneimine was a medium which grafted graphene oxide onto surface of carbon fiber by chemical bond; identified the optimal reaction concentration, reaction time and reaction method of graft reaction by SEM; the surface energy test suggested that the introduction of graphene oxide improve the wettability of carbon fiber with polymer matrix by 47.08% ; interface shear strength test showed that after grafting graphene oxide, the interface strength of carbon fiber and matrix increased by 18.44%.

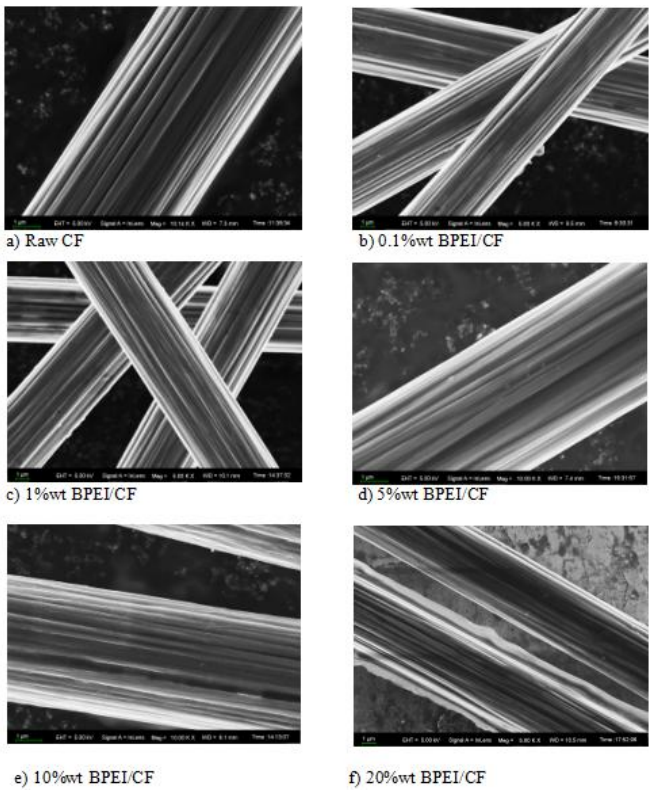
At present, in the study of carbon fiber hierarchical reinforcement, the researchers have successfully introduce graphene oxide to the carbon fiber's surface. Compared with those of other reinforced material, the high specific surface area of graphene oxide can have more sufficient contact with the matrix, and the large amount of oxygen-containing groups on surface make it has very good wettability in polar polymer matrix, which can greatly improve the interface state.All of the preparation methods of carbon fiber hierarchical reinforcement have certain deficiencies, in order to increase the content of active functional groups on the surface of carbon fibers, many researchers grafted moleculars which have a large number of reactive amino groups onto the carbon fiber's surface through amide reaction. However, the peptide condensation reagents required for the amide reaction usually have strong toxicity, the reaction time is long and the reaction process is also complicated. Therefore, my research want to modify carbon fiber's surface by a more environmentally friendly, convenient and rapid way, to improve its surface energy and interface strength.

This research proposed two new hierarchical reinforcement, one is BPEI grafted CF, And the other is GO grafted CF. I raised the physical compatibility and chemical compatibility of carbon fiber and epoxy resin matrix, and explored the enhancement mechanism of the interface.

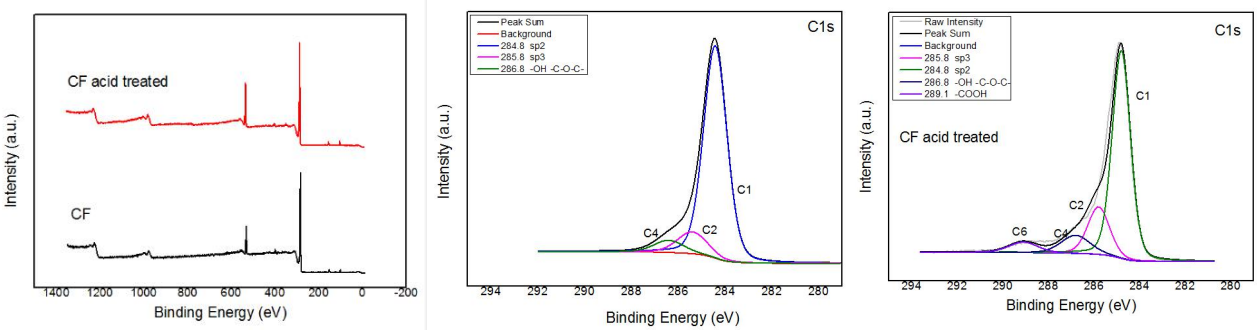
Firstly, I will introduce BPEI grafted carbon fiber hierarchical reinforcement. In this paper, nitric acid was used to oxidation etch the carbon fiber, and hydroxyl and carboxy groups were introduced into it. The protonated amino of BPEI reacted with hydroxyl to form hydrogen bond and reacted with carboxyl to form ionic bond. Epoxy groups can anchor BPEI on the surface of carbon fiber. The increase of epoxy group can directly improve the anchoring effect of BPEI.



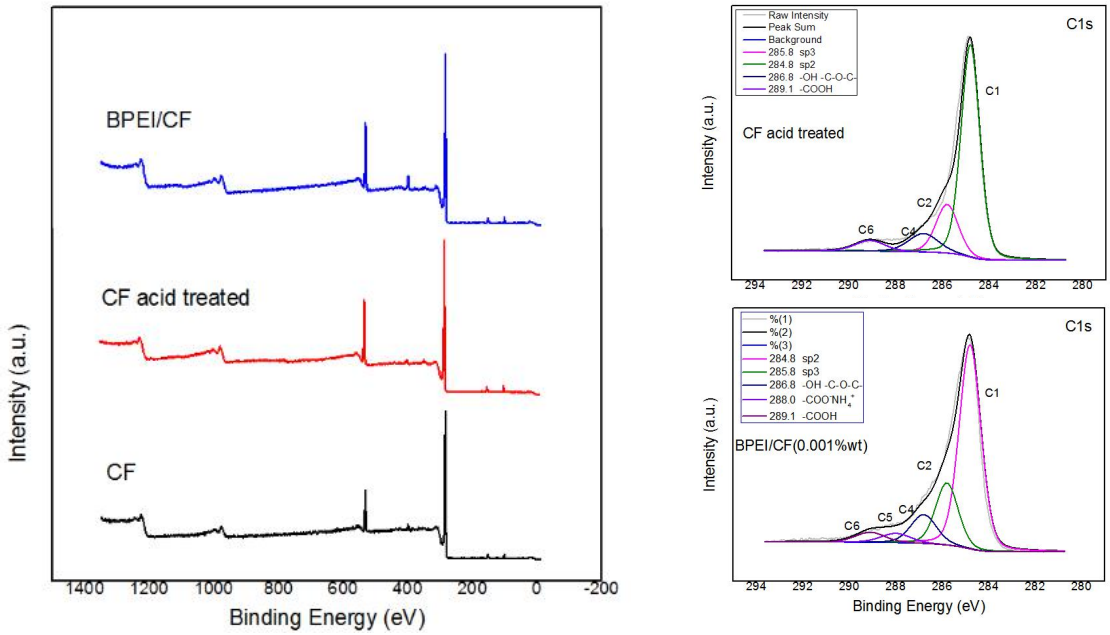
Here are The SEM micrographs of five different grafting concentrations. When the mass concentration of BPEI was 0.1% or 1%, the surface morphology of the reinforcement did not differ from that of the raw fiber. When the mass concentration was 5% or 10%, A layer of film wraps over the surface of the fiber, and the groove is no longer as clear as the original. Until the mass concentration reaches 20%, the translucent film is clearly visible and the grooves on the fibers are also filled with BPEI molecules.



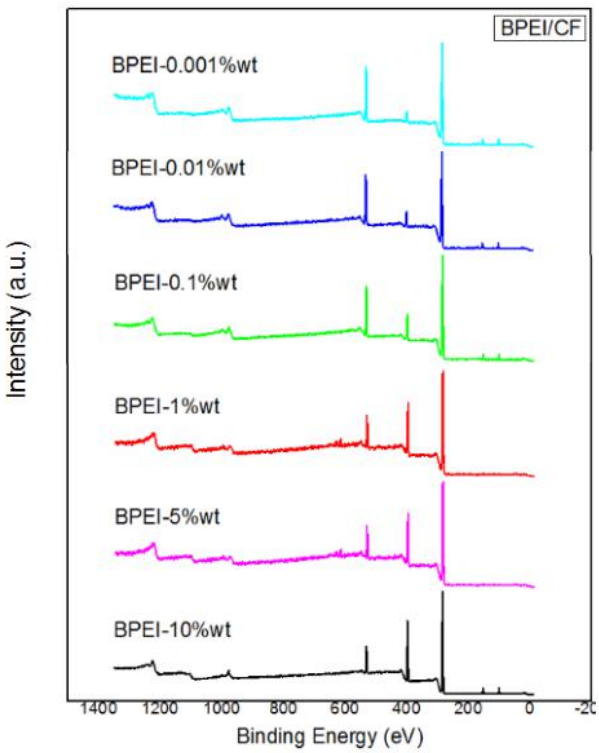
The raw fiber and the fiber oxidized by concentrated nitric acid were characterized by XPS. It was found that the oxygen content of carbon fiber increased obviously after oxidation. After peak-differentation-imitating, we can find that, after oxidation, there is a new fitting curve at 289.1 electron volt, Corresponds to carbon atoms in carboxyl, which indicated that the oxidation of concentrated nitric acid could introduce carboxyl group into carbon fiber surface.

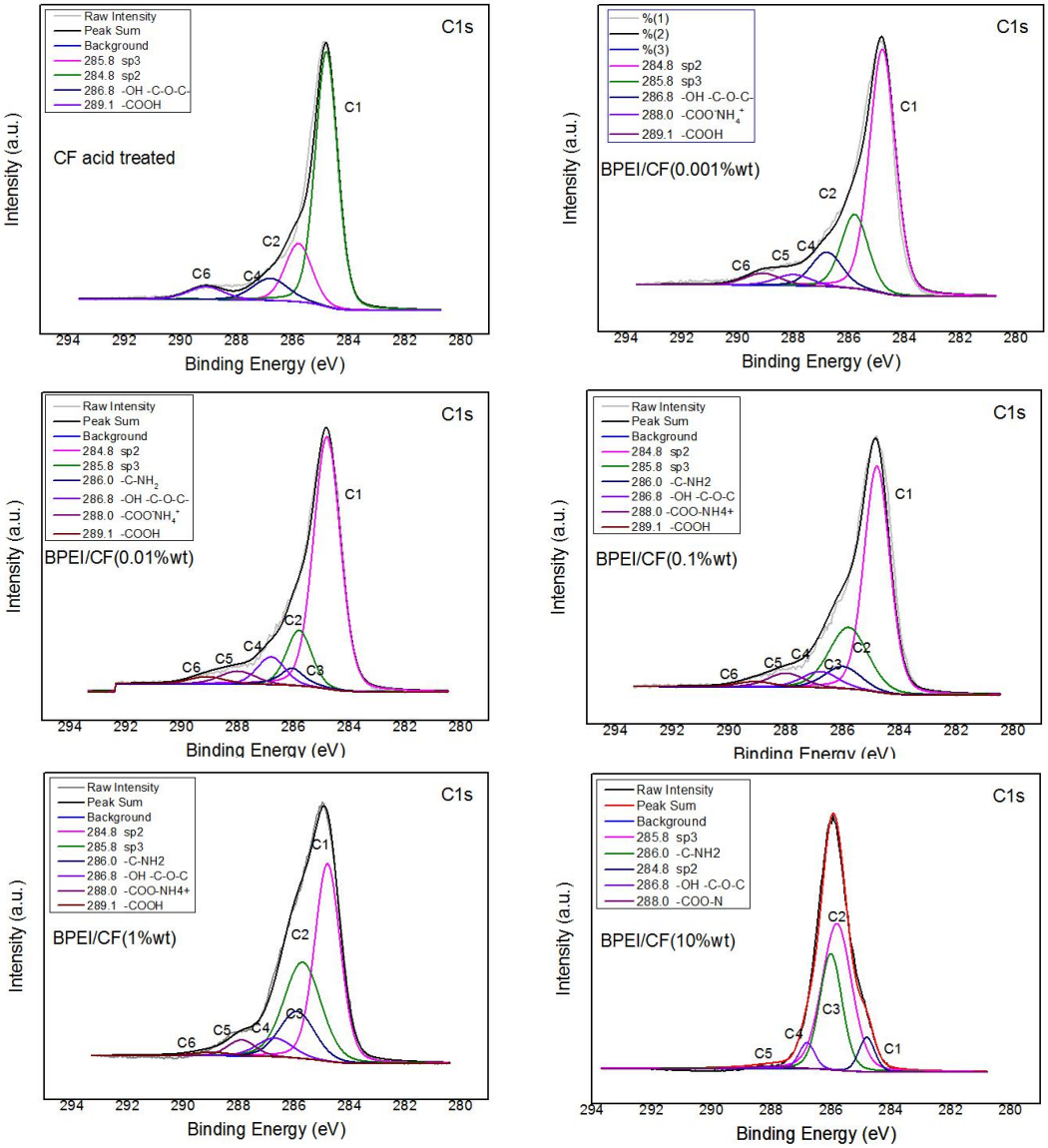


Compared with the BPEI grafted carbon fiber hierarchical reinforcement, we can find the content of nitrogen was obviously increased. It can be seen that, compared with the carbon fiber after the oxidation of the nitric acid. a new peak appeared at 288.0 electron volt after reaction with BPEI molecule, it' s the peak of the ionic bond. It was confirmed that the BPEI grafted carbon fiber process is a chemical reaction process, The reaction forms a new chemical bond.



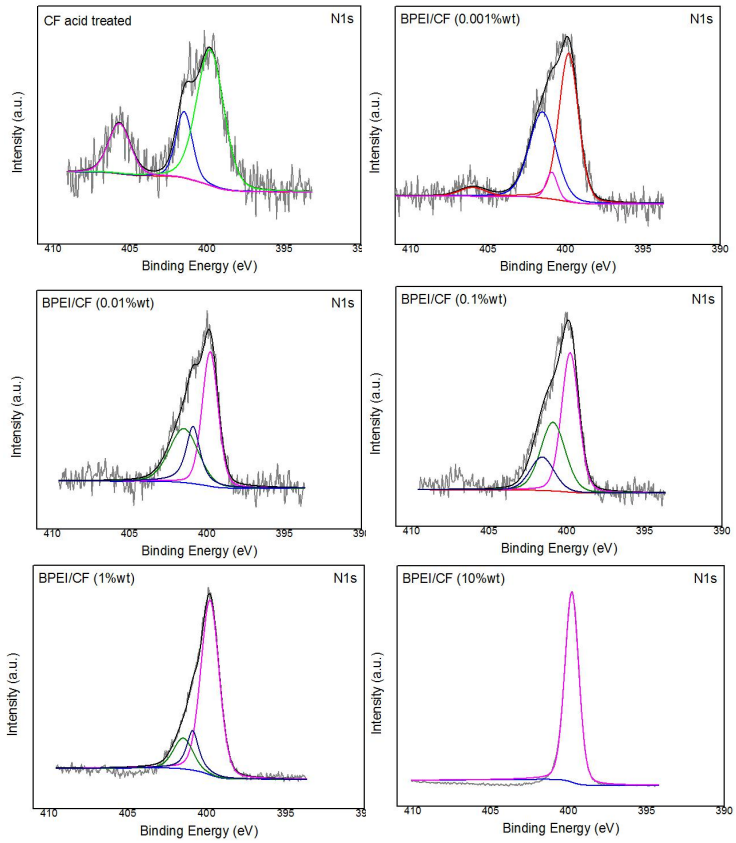
The XPS spectra of six groups of different grafting density indicated the content of nitrogen functional groups on the surface was significantly increased. When The grafted concentration is 0.1per thousand, the content of amino on surface is zero, because when the graft concentration is low, all Amino groups on BPEI molecular chain react with hydroxyl and carboxyl ion on carbon fiber's surface , The reaction forms new chemical bonds. When the grafting concentration gradually increased, the content of Amino groups increased.





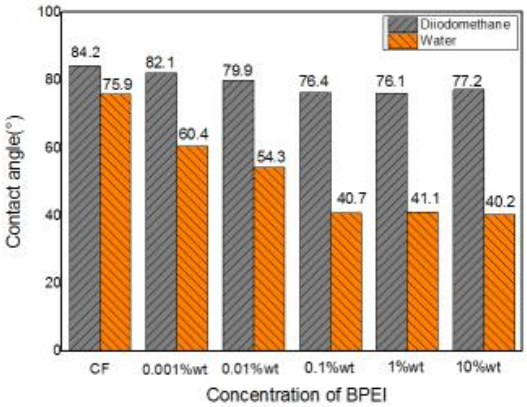
BPEI（%wt）	C-sp2	C-sp3	$-C-NH_2$	-OH、-C-O-C-	$-COO^-NH_4^+$	-COOH
0.001	64.28	19.59	—	8.38%	3.85%	3.89%
0.01	59.60	21.49	3.66%	7.49%	4.58%	3.18%
0.1	54.53	23.80	7.93%	6.82%	5.02%	1.89%
1	44.18	31.00	14.32%	5.73%	3.89%	1.15%
10	6.86	54.55	32.59%	5.03%	0.98%	—

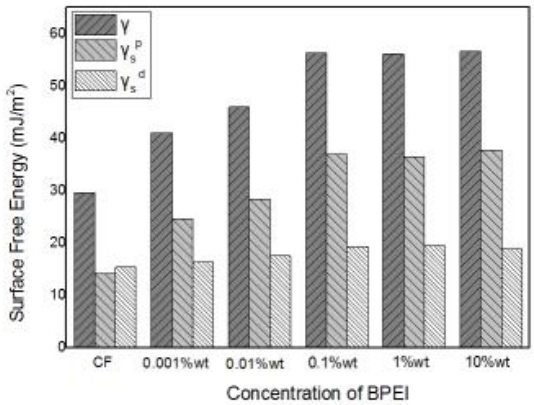
Observe the trend of relative content of -COO^- $NH4^+$ and -COOH, we can find that when the grafting concentration is 0.1%, the content of COO^- $NH4^+$ is highest. When the concentration continued to increase, The relative content of ionic bonding decreased. Because the outer molecular gradually covered with the first layer of molecules which reacted with the carboxyl groups on carbon fiber's surface, and the outer molecular became more and more. Therefore, when the graft concentration is 10%, the layer of BPEI molecular membrane became thicker, the content of sp^2 hybrid structure is reduced to 6.86%, the content of carbon-carbon bond and amino groups of grafting molecule increases to 54.55 % and 32.59%, at this time, the carbon fiber surface was unable to detect the presence of carboxyl. The N1 peak curves of the six groups showed that when the grafting density increased gradually, the carbon-nitrogen bond peak at 399.8 electron volt gradually increased, because the number of BPEI molecules on the carbon fiber surface increased gradually. And the content of COO^- $NH4^+$ was the highest when the concentration of BPEI was 0.1% wt, which was consistent with the above conclusion. So The optimal reaction concentration of BPEI was 0.1%.



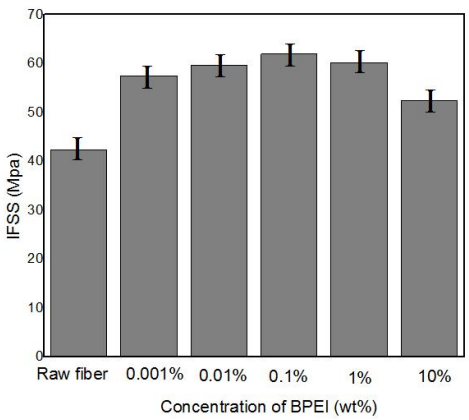
BPEI （%wt）	C-N (399.8eV)	$COO^-NH_4^+$ (400.9eV)	$C-N^+$ (401.5eV)	$-NO_3^-$ (406.0eV)
0 (CF)	62.65%	—	18.47%	18.88%
0.001	49.45%	5.29%	39.93%	4.04%
0.01	45.35%	21.56%	33.09%	—
0.1	48.39%	35.08%	17.82%	—
1	72.46%	13.85%	13.58%	—
10	100%	—	—	—

This research used dynamic contact angle test to measure the contact angle of raw carbon fiber and BPEI grafted carbon fiber in diiodomethane and water. It was found that the contact angle in diiodomethane decreased slightly with increasing BPEI concentration, while the contact angle in water decreased greatly with the increase of concentration. When the grafting density reached 0.1%, The effect of grafting density on the contact angle disappeared. At the same time, we found that after grafting, the surface energy of the carbon fiber hierarchical reinforcement obviously increased. With the increase of the concentration of BPEI, the polar component increased. When the mass concentration of BPEI reached 0.1% wt, the surface polarity no longer changed. because the number of the functional groups on the outermost layer remained constant, so the polarity strength trend to stable. However, the change of dispersive component is not obvious, because the nanometer scale of BPEI molecule makes little contribution to carbon fiber's surface roughness and specific surface area.





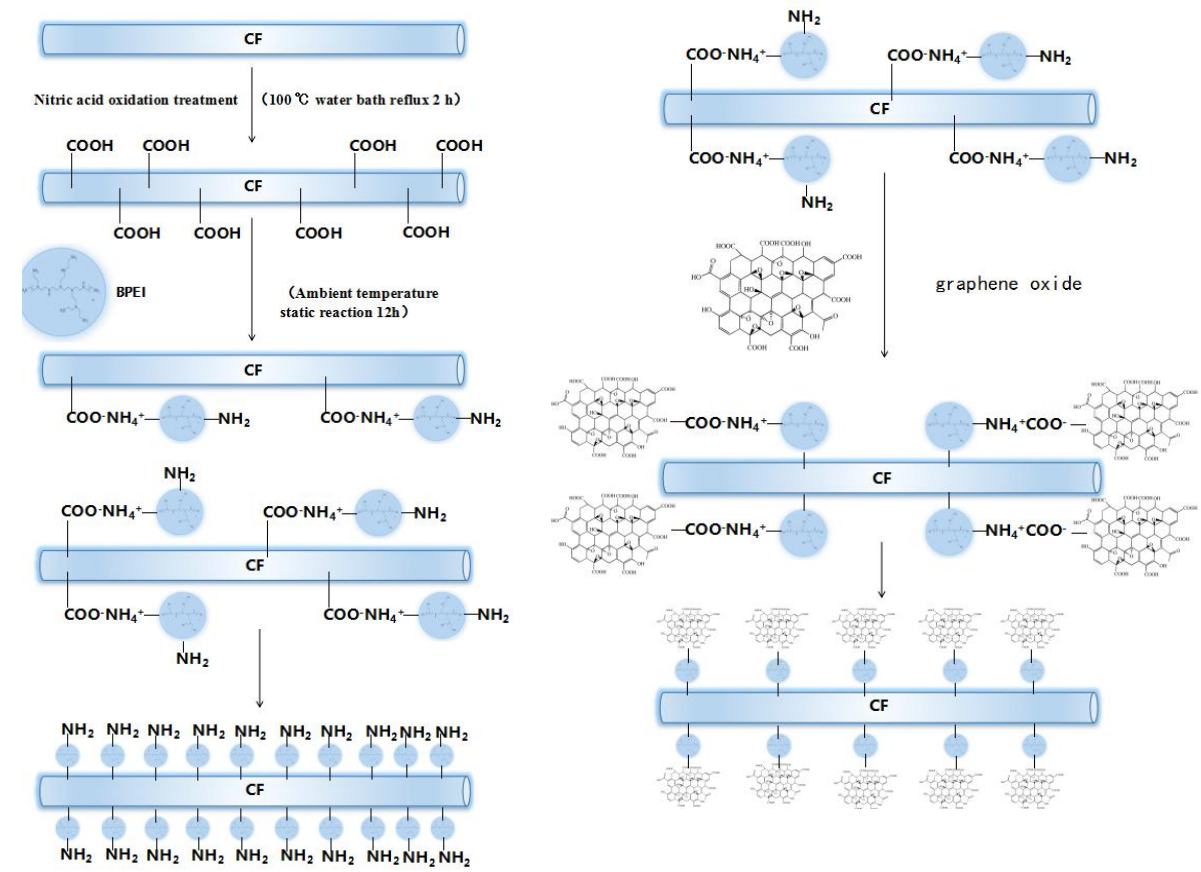
The interfacial shear strength of BPEI grafted carbon fiber was tested by micro droplet bonding test. The results showed that compared with the raw carbon fiber, the interface strength first increase and then decrease when the grafting density of BPEI was increased. The highest enhancement is 46.34%. Because, with the gradual increase of BPEI molecules grafted on the surface of carbon fiber, the number of chemical bonds between resin matrix and carbon fiber increased, the good wettability and chemical bonding at the interface make the composite material's destruction no longer because of bonding failure, but because of The cohesive failure of the matrix, thus, the interface strength was improved.



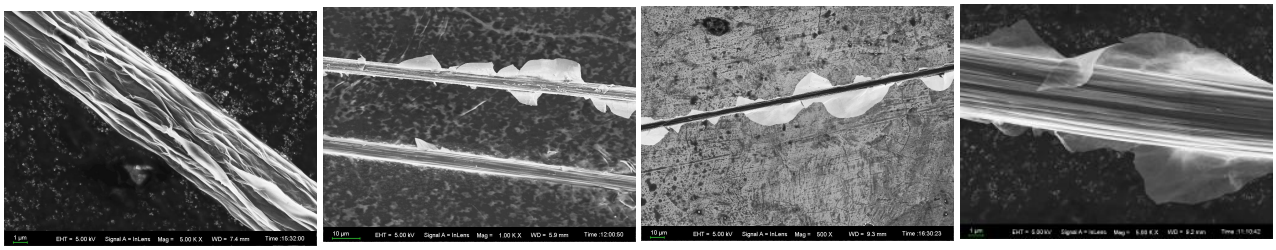
When the grafting concentration increased to 0.1%, the molecules have covered with the carbon fiber's surface. And then The increase of BPEI molecules caused the stacking of excess molecules. They adsorbed onto the first layer of BPEI on the carbon fiber surface through the van der Waals force. Then the mode of destruction is changed from cohesive failure of epoxy resin to overcome van der Waals force of BPEI, thus the interfacial strength is weakened. It was also demonstrated that the monomolecular structure had the greatest influence on the interfacial strength when BPEI was grafted.

In the first part of research, I successfully prepared BPEI grafted CF hierarchical reinforcement, BPEI and CF are connected by chemical bonds. The surface energy is increased by 90.05%. And the introduction of BPEI enhances the polarity component. The interfacial strength increased by 46.34%. And The optimum grafting concentration was 0.1%.

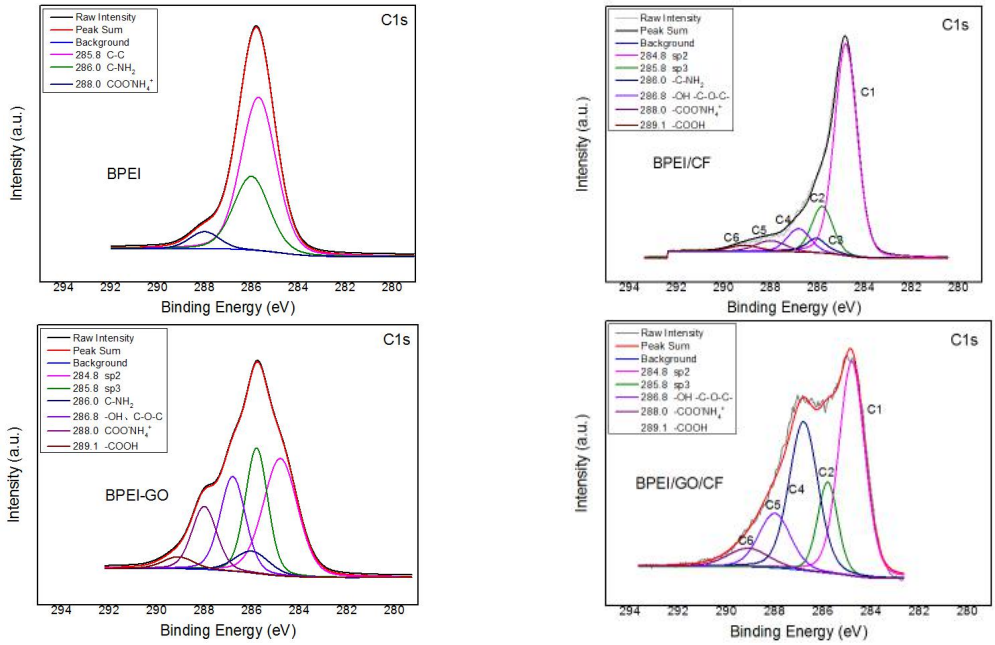
The second part is a description of graphene-oxide grafted carbon fiber hierarchical reinforcement. The surface of GO has a large number of oxygen-containing functional groups, On the basis of the study of BPEI grafted carbon fiber reinforcement, I grafted GO onto the surface of carbon fiber by the reaction of a large amount of amino groups of BPEI molecule and the epoxy group of the graphene oxide.



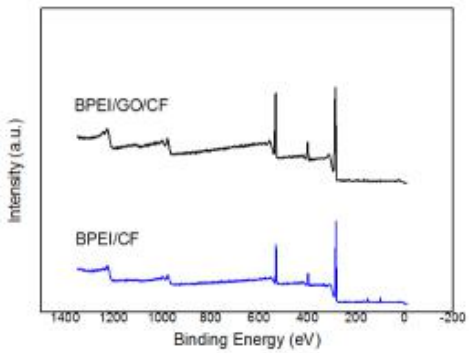
In order to obtain the GO grafted carbon fiber hierarchical reinforcement with good microstructure, my research discussed and regulated the reaction’ s mode, time and concentration of BPEI and graphene oxide. The results shows that, The optimal reaction concentrations of BPEI and GO were found to be 1% and 1 milligram per milliliter respectively. And the reaction is able ro complete within 10 seconds.



In order to verify that BPEI can form chemical bond with GO, I characterized the reinforcement by XPS. The following figure shows the peaks of carboxyl, hydroxyl and ether linkages. At 288.0 electron volt, the content of COO^{-} $NH4^{+}$ increased from 5.98% to 13.87%, and the relative content of amino groups decreased from 30.77% to 6.63%, which was due to the protonated BPEI molecules in solution and the carboxyl group in graphene oxide were com bined by electrostatic interaction. It was confirmed that the process of combining the GO with BPEI was a chemical reaction process, and the reaction formed new chemical bonds.

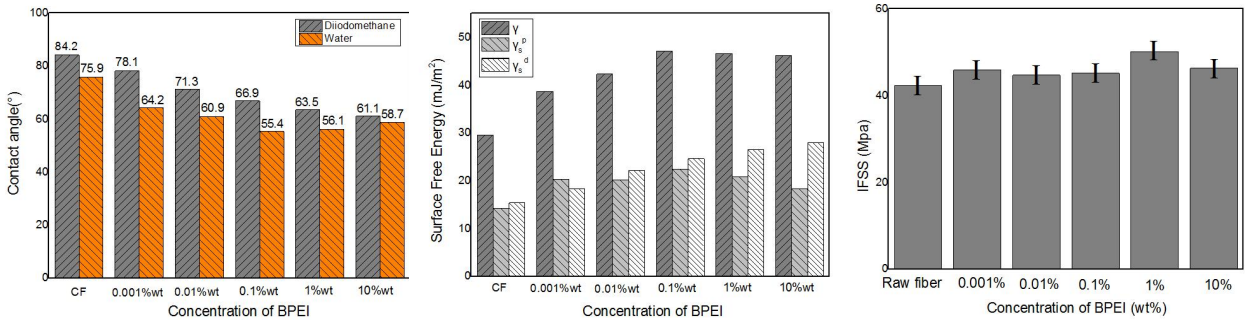


It can be seen that the Nitrogen and oxygen ratio of BPEI grafted carbon fiber reinforcement is Significantly lower than GO grafted carbon fiber reinforcement, because the amount of functional groups is greatly increased when the graphene oxide is grafted onto the surface of the carbon fiber. Obviously, graphene oxide has been successfully grafted onto the surface of the carbon fiber.



The surface energy of carbon fiber hierarchical reinforcement is increased by 59.16% by the introduction of GO. The carboxyl and hydroxyl groups increase the polarity of carbon fiber reinforcement by 58.35%, and its rough surface and high specific surface area make the dispersive component of the carbon fiber reinforcement increased by 81.55%.

The interface shear strength was increased by 18.44% after grafting GO. Because the GO sheets on the interface can be deep inside the epoxy resin, and GO can optimize the infiltration of carbon fiber and resin, it lead to a good physical combination of resin matrix and carbon fiber. The fracture of the composite materials have a greater chance of cracking from the interface to internal expansion of the epoxy matrix, therefore, the interface strength can be improved.



In the second part of research, I Successfully prepared GO grafted CF hierarchical reinforcement, the Surface energy improved by 59.16%. Both the dispersive component and the polarity component are enhanced. And The interface strength increased by 18.44%. This reaction process is Environmentally friendly, simple and fast.