

Surface Characteristics of Rare Earth Treated Carbon Fibers and Interfacial Properties of Composites

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Abstract: Effect of rare earth treatment on surface physicochemical properties of carbon fibers and interfacial properties of carbon fiber/epoxy composites was investigated, and the interfacial adhesion mechanism of treated carbon fiber/epoxy composite was analyzed. It was found that rare earth treatment led to an increase of fiber surface roughness, improvement of oxygen-containing groups, and introduction of rare earth element on the carbon fiber surface. As a result, coordination linkages between fibers and rare earth, and between rare earth and resin matrix were formed separately, thereby the interlaminar shear strength (LSS) of composites increased, which indicated the improvement of the interfacial adhesion between fibers and matrix resin resulting from the increase of carboxyl and carbonyl.

Key words: carbon fiber/epoxy composite; interfacial properties; X-ray photoelectron spectroscopy; rare earths

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Polymer matrix composites are the main application of carbon fibers. The interface between the carbon fibers and the resin matrix plays a critical role in controlling the overall properties of the composites, such as, off-axis strength, fracture toughness, and environment stabilities. Interfacial characteristics determine the path by which loads can be transferred from polymer to fiber, and are often quantified in terms of the so-called interlaminar shear strength (LSS). Below a certain critical strength, the surface of the fibers is not sufficient for the transfer to occur adequately. However, the inertness characteristic of the carbon fiber surface usually results in inferior wettability and weak adhesion between the fibers and resin^[1-3]. As a result, it is necessary to treat or modify the surface of carbon fibers in their application.

A literature survey shows that a range of experimental techniques have been applied to modify the

surface of carbon fibers, including anodization, plasma treatment, and solution and gas phase oxidation^[1, 4-7]. Most modifications on the interfacial properties of carbon composites have been focused on increasing the surface free energy or introducing organic groups on the fibers, moreover, the interfacial property was improved at all levels after modification.

Rare earth compounds have been widely used in optics, electronics, metallurgy, and chemical engineering because of their special characteristics^[8-13]. During the past few decades, most investigations have focused on the effect and application of rare earth elements on the metal surfaces, and a few are related to using rare earth elements as nonmetal material surface modifiers^[14-18]. In particular, less information is available on the application of rare earth elements for surface treatment of carbon fiber, as well as the effect of rare earth elements on the adhesive property of car-

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bon fiber composites. In this study, it is indicated that rare earth treatment has the virtue of higher efficiency, lower facilities, and lower maintenance cost, compared to other methods. Therefore, an attempt has been made to improve the physicochemical properties of the carbon fiber surface by rare earth treatment.

The purpose of the present study is to evaluate the surface treatment of carbon fibers by means of $\text{Pr}(\text{NO}_3)_3$ solution, investigate the effect of different rare earth concentrations on the interfacial properties of carbon/epoxy composites and relate them to the interfacial behavior in polymer matrix composites.

1 Experimental

1.1 Preparation

Polyacrylonitrile (PAN) based carbon fibers with kidney-type cross section, investigated in the current studies were supplied by Institute of Coal Chemistry, affiliated to the Chinese Academy of Sciences. The average width of the fiber section was $9\ \mu\text{m}$, the thickness was $3\ \mu\text{m}$, and the linear mass of the fiber was $0.0627\ \text{g}\cdot\text{m}^{-1}$. Praseodymium nitrate was prepared by dissolving praseodymium oxide (purchased from Shanghai Chemical Reagent Co.) in nitric acid. The matrix system used was E-618 epoxy resin system consisting of diglycidyl ether of bisphenol-A (supplied by Yue-Yang Chem. Co. of China), curing agent phthalic anhydride, and benzyl dimethylamine at 100, 70, and 1 part by mass, respectively.

Three types (0.1%, 0.5%, and 5%, mass fraction) of $\text{Pr}(\text{NO}_3)_3$ water solution were used. Before treatment, the fibers were put in a plastic container and vacuumized. Then praseodymium nitrate/water solution was inhaled into the container under negative pressure, and the fibers were wholly immersed. The carbon fibers were dipped into the solution of $\text{Pr}(\text{NO}_3)_3$ for 6 h, and then dried for 2 h at 120°C .

Using the carbon fibers and epoxy resin, the prepreg was paid unidirectional into a mold to manufacture composites. The prepreg was pressed and cured under 5 MPa pressure for 2 h at 90°C , under 10 MPa pressure for 2 h at 120°C , and under 10 MPa pressure for 4 h at 160°C by hot-press machine and the authors could obtain specimens with a fiber mass fraction of $64(\pm 1\%)$.

1.2 Measurement

Atomic force microscope (AFM) (Nanoscope) made in America, Digital Instrument Company, was employed to observe the surface topography of fi-

bers. The morphology of the failure of fiber-reinforced composites was inspected with the help of a scanning electron microscope, (SEM) FEI SIRDON 200, before and after treatment. ESCA (Lab220i-XL) made in V. G. Scientific Company, U. K. and equipped with an Al K ($1.25\ \text{keV}$) radiation source generated at 12 kV and 20 mA, was used to determine the composition of fiber surface. Before the X-ray photoelectron spectroscopy (XPS) test, untreated and treated carbon fibers were both extracted with acetone for 48 h, to wash out the impurities on their surface.

The LSS of composites was measured by the short-beam bending test according to ASTM D-2344 using Instron 1125. A span-to-depth ratio of 5:1, a crosshead speed of $2\ \text{mm}\cdot\text{min}^{-1}$, and a sample thickness of 2 mm were used. More than eight specimens were tested for each of the composites studied and the average value was taken from the present study.

2 Results and Discussion

2.1 Surface topography of fibers

The AFM images of the original and treated carbon fibers are shown in Figs. 1(a~d). The striatures are generated by alignment of the regularly lined up carbon atoms rings, along the longitudinal direction of the fiber. Compared to the original carbon fiber, the treated carbon fiber surface is rougher, and the grooves on the fiber surface become wider and deeper. The mean surface roughness of the original, 0.1% rare earth treated, 0.5% rare earth treated, and 5% rare earth treated carbon fibers is 128.7, 130.6, 138.4 and 135.3 nm, respectively. Moreover, carbon fibers treated with high concentration solution show a more distinct increase in roughening and depth of grooves than the fiber treated with low concentration. It indicates that the praseodymium ion etches the carbon fiber surface properly in 0.5% rare earth solution and excessively in 5% rare earth solution.

2.2 Surface composition of fibers

It is well known that XPS is a very useful technique in the determination of chemical composition and functional groups of the fiber surface, and the maximal XPS sampling depth is $\sim 6\ \text{nm}$. Wide scan spectra in the binding energy range $0\sim 1400\ \text{eV}$ are obtained to identify the surface elements present and carry out a quantitative analysis. The XPS spectra show distinct carbon and oxygen peaks, representing the major constituents of the carbon fibers investigated. Praseodymium and nitrogen elements are detected

from the spectroscopy of carbon fibers treated. A small amount of silicon is also observed as an impurity. The surface composition of untreated and treated carbon fibers determined by XPS is given in Table 1.

As shown in Table 1, the amount of surface oxygen increases, the amount of surface carbon decreases, and the elements of praseodymium and nitrogen are detected after rare earth treatment.

Figs 2 (a ~ d) presents C_{1s} envelopes for the virgin and treated fibers. It is noticed that the total fraction of C_{1s} envelope associated with oxygen environments (shoulders locate on the high energy side of the main peak at 284.8 eV) is greater for samples processed by rare earth treatment. However, XPS is not capable of resolving the individual contributions of functionalities, such as, hydroxyl-ester, carbonyl, carboxyl, anhydrides or lactose. Following a previous study in the literature^[19], a semi-quantitative description of the differences was attempted using the curve-fitting deconvolution procedure. The carbon peaks observed in the binding energy range from 280 to 295 eV. This can be attributed to several carbon-based surface functional groups that have different binding energies. The C_{1s} peak of each carbon fiber sample has been analyzed using the peak synthesis

Table 1 Variation of surface composition of carbon fibers after treatment (% , mass fraction)

Fiber	C	O	Pr	N	Si
Untreated	85.42	11.61	0	0	2.97
0.1% treated	67.82	24.45	0.83	2.41	4.49
0.5% treated	54.93	34.78	1.77	4.08	4.44
5.0% treated	50.56	33.49	5.88	6.80	3.27

procedure, which combines Gaussian and Lorentzian functions. The intensity contribution of each functional component peak has been estimated by computer simulation^[20, 21].

The narrow scan spectra of the C_{1s} region deconvoluted into the surface functional group, and contributions are shown in Figs 2 (a ~ d) for the untreated, 0.1% rare earth treated, 0.5% rare earth treated, and 5% rare earth treated carbon fibers, respectively. The binding energy value and percent contribution of each curve fit photopeak is estimated from these curve fit C_{1s} photopeaks and they are listed in Table 2. Deconvolution of the C_{1s} spectra of carbon fibers gives four peaks designated as peak 1 (at 284.5 ~ 284.9 eV assigned to graphitic carbon), peak 2 (at 285.5 ~ 285.8 eV, carbon bonded phenolic, alcoholic hydroxyls or ether oxygens), peak 3 (at 286.7 ~ 286.9 eV, carbonyl carbon

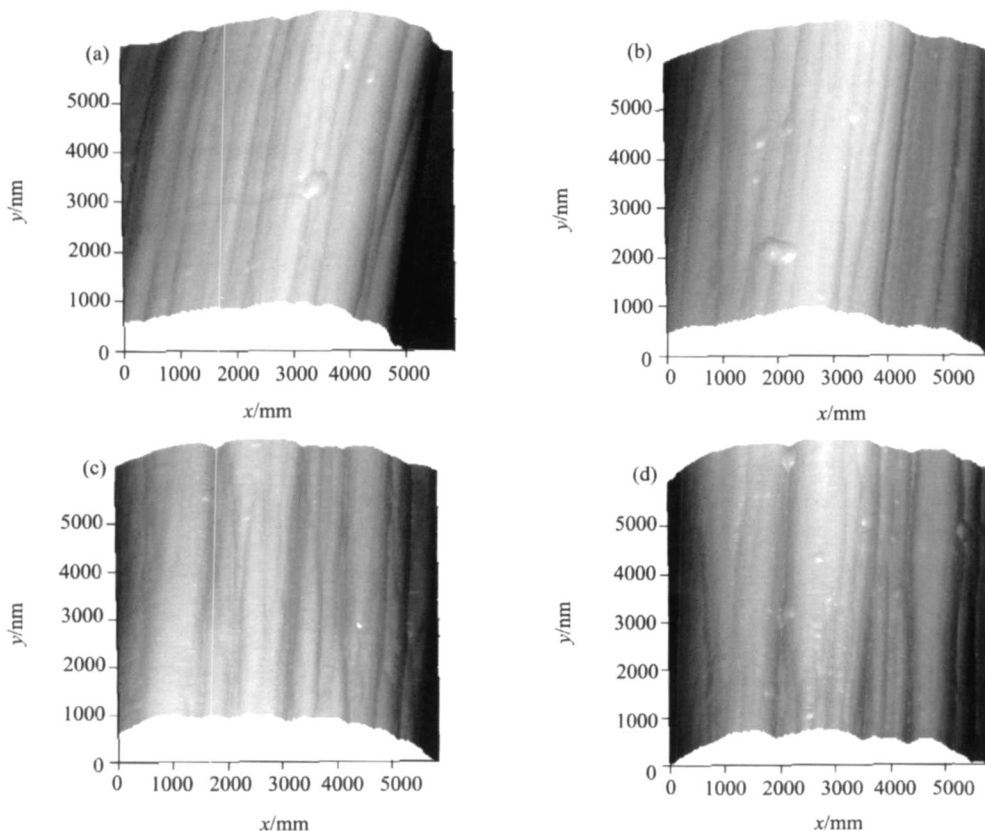


Fig 1 Three-dimensional topography of carbon fiber surface
(a) Untreated; (b) 0.1% rare earth treated; (c) 0.5% rare earth treated; (d) 5% rare earth treated

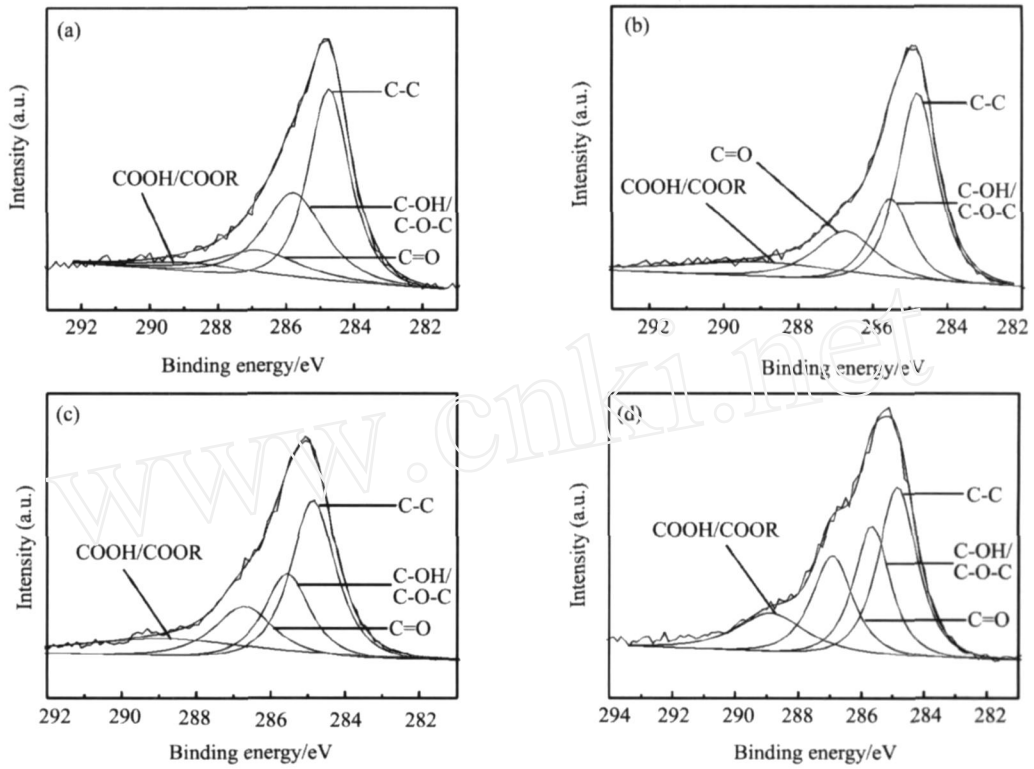


Fig 2 C_{1s} XPS spectra of carbon fibers untreated and treated (a) Untreated; (b) 0.1% rare earth treated; (c) 0.5% rare earth treated; (d) 5% rare earth treated

Table 2 Relative content of functional groups in C_{1s} spectra from XPS (% , mass fraction)

Fiber	C - C	C - OH/C - O - C	C = O	COOR / COOH
	284.5 ~ 284.9	285.5 ~ 285.8	286.7 ~ 286.9	288.7 ~ 289.0
Untreated	49.7	31.9	12.9	5.5
0.1%	46.5	20.2	18.5	14.8
0.5%	42.3	22.5	17.8	17.4
5.0%	37.2	25.4	22.1	15.3

in ketones and quinines), and peak (at 288.7 ~ 289.0 eV, carboxyl functions or ester groups)^[22-24].

Close examination of the graphite carbon peak shows that the full width at half maximum (FWHM) increases from about 1.4 eV for the original carbon fibers to 1.48 eV for the 0.5% rare earth treated carbon fibers, suggesting that disordering of the carbon lattice might result from treatment. This also indicates that higher microporosity is correlated to decreasing graphitic character of the surface region^[25].

From these results in Table 2, it is clear that in the carbonyl carbon in ketones and quinines (C=O) and carboxyl functions or ester groups (COOH/COOR), the functional groups increase, and the graphitic carbon (C-C) and carbon bonded phenolic or alcoholic hydroxyls or ether oxygen (C-OH/C-O-C) functional groups decrease after treatment.

2.3 Interfacial properties of composites

The LSS results of composites reinforced by carbon fibers treated in different concentrations are shown in Fig 3. After surface treatment, the LSS values of composites are enhanced by 10.1% (0.1% rare earth) and 15.3% (0.5% rare earth), respectively, compared to the untreated carbon fiber composites. The chemical bonding and mechanical interlocking between carbon fibers and matrix resin may be responsible for these results. However, the treatment of 5% rare earth leads to a 7.4% decrease of LSS value. It may be because of the influence of excessive praseo-

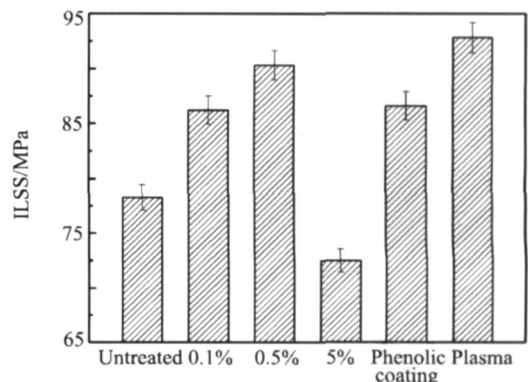


Fig 3 Effect of treatment methods on LSS of carbon fiber/epoxy composites

dymium ions and nitrate ions on the reaction between the epoxy resin and functional groups on the fiber surface. In addition, the excessive praseodymium ion infiltrates easily into the resin matrix and hampers the curing reaction of the matrix. It is indicated that rare earth treatment at the proper concentration is beneficial for improving the interfacial adhesion of carbon fiber/epoxy composites, and excessive rare earth treatment will not achieve a good interface between the carbon fiber and matrix.

Fig 3 also presents the LSS of phenolic-coated carbon fiber/epoxy and plasma treated carbon fiber/epoxy. It is noted that 0.5% rare earth treatment performs better than phenolic coating. Plasma treatment outperforms rare earth treatment marginally, but it is difficult to use for applications because of its low facilities and high maintenance cost.

2.4 Fracture surface topography of composites

Representative topographic fracture features of untreated and rare earth-treated carbon fiber/epoxy composites are shown in Fig 4. There is a marked difference in surface topography between untreated and treated fiber composites. From the figures, it can be seen that the fracture surface of the composite with untreated carbon fiber exhibits a detached appearance and poor interfacial bonding. The fibers are separated from the resin matrix (Fig 4(a)). The interfacial bonding of composites with 0.1% rare earth treated carbon fibers appears to have obviously improved, as can be seen in Fig 4(b). The composites employing 0.5% rare earth treated carbon fibers show less fiber split and the matrix is engulfed by fibers. This allows the matrix to secure more bonds and have a better adhesive force between two phases, which can effectively transfer the load applied to the fiber-reinforced composite system (Fig 4(c)). Nevertheless, the 5% rare earth treatment is not rewarded by the superior adhesion between fibers and resin (Fig 4(d)).

2.5 Mechanism of interfacial adhesion improvement

According to the chemical bonding theory and the

interdiffusion theory, the praseodymium ion is absorbed onto the carbon fiber surface through chemical bonding, which increases the concentration of the reactive functional groups because of the chemical activity of the rare earth element. These reactive functional groups can improve the compatibility and reaction between the carbon fibers and the epoxy matrix and form a chemical combination between the carbon fibers and epoxy matrix. Therefore, increasing the amounts of oxygen-containing functional groups on the fibers plays an important role in improving the degree of adhesion at the interfaces (hereby, Keesom's attraction of van der Waals force, hydrogen bonding, and other small polar effects) between fibers and matrix, and the LSS of the resulting composites is enhanced^[20].

Second, the rare earth ion adsorbed onto the fiber surface forms a coordinate bond between fibers and matrix, and acts as a bridge connecting carbon fibers to the matrix resin^[26~29]. A schematic diagram is shown in Fig 5.

In addition, when carbon fibers are soaked in rare earth solution, the fiber surface becomes rougher. Increase of fiber roughness and surface striations can promote mechanical keying or interlocking between fibers and matrix^[5]. As a result, interfacial adhesion of carbon fiber/epoxy composites is improved through rare earth surface treatment.

3 Conclusions

1. The surface of treated carbon fiber was rougher and some grooves were formed compared to the original carbon fiber.

2. On the surface of treated carbon fibers, praseodymium was detected. The carbonyl carbon in ketones and quinines ($C=O$) and carboxyl or ester ($COOH/COOR$) functional groups increased, and the graphitic carbon ($C-C$) and phenolic or ether oxygen ($C-OH/C-O-C$) functional groups decrease.

3. LSS of the composites, including 0.5% rare earth-treated carbon fibers showed about a 15.8% improvement compared to that of composites employing nonsurface treated carbon fibers. This could be attrib-

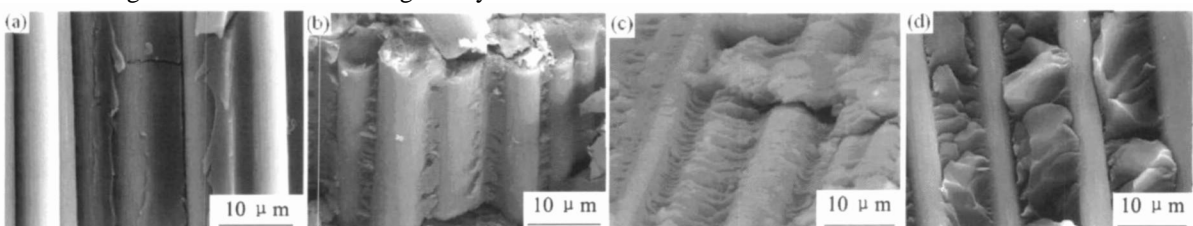


Fig 4 SEM micrographs of fracture surface of composites
(a) Untreated; (b) 0.1% rare earth treated; (c) 0.5% rare earth treated; (d) 5.0% rare earth treated

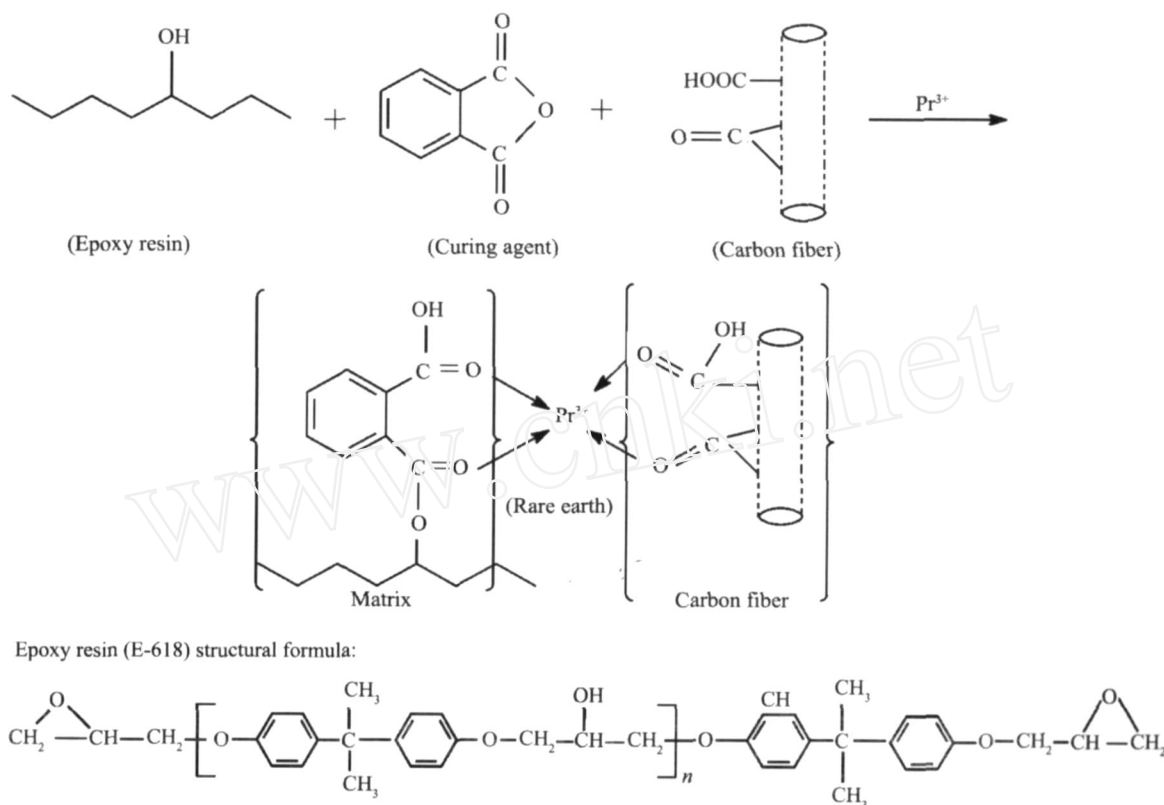


Fig 5 Schematic diagram of coordination linkage between carbon fibers and matrix resin

uted to the increase of oxygen groups, coordination linkage between fiber and matrix, and improvement of roughness

4. The composites employing 0.5% rare earth treated carbon fiber showed less fiber split and the matrix is engulfed by fibers

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