Preparation and properties of chopped carbon fiber reinforced PEEK composites

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ABSTRACT

Chopped carbon fiber reinforced PEEK [poly(ether-ether-ketone)] composites were manufactured by electromagnetic effect mixing technology and thermal pressure molding technology. The chemical structure and properties of chopped CF/PEEK composites were characterized by infrared spectrometry (IR) analysis, thermo gravimetric Analysis (TGA), coefficient of thermal expansion (CTE), mechanical tests and scanning electron microscopy (SEM). The results showed that the PEEK chemical composition of CF/PEEK composites was stable in the hot-pressing and oxidative decomposition did not occur. PEEK heat resistance did not decrease with the adding of chopped CF, and could be enhanced by 5K containing 10% (mass fraction) chopped CF. The CTE of chopped CF/PEEK composites decreased with the rise of chopped CF content, and changed a little in the temperature range of (-150℃~140℃) and (170℃~260℃). From room temperature to 275℃, the specific heat capacity （C_p） of PEEK and chopped CF/PEEK composites both presented with approximately linearly increasing, but the C_p of CF/PEEK composites jumped in the temperature of (300℃~330℃) due to PEEK's physical state changing from glass state to plastic state, in addition, the C_p decreased with enhancing chopped CF content. The heat conductivity (λ) and thermal diffusion coefficient (α) increased with increasing CF content. The compress strength and compress modulus had the trend of rise-fall with increasing CF content, the maximum value was 303MPa and 3.69GPa with 10% (mass fraction) chopped CF respectively. It could be obtained that PEEK had good compatibility with chopped CF through the SEM photos, and the fracture images of compression specimens appeared typical super spherical fractures.

1 INTRODUCTION

PEEK [Poly(ether-ether-ketone)] is a kind of engineering thermoplastics with linear aromatic semi-crystalline chemical structure. As rigid benzene ring, soft carbonyl group and ether linkage in the molecular chain, PEEK polymer have excellent mechanical property, chemical resistance, good fatigue property and heat resistance (continuous operating temperature above 250℃)[1,2]. Compared with thermosetting composites, CF/PEEK composites are also used in a large number of structures, especially aerospace industries. As structural component, it can afford many excellent physical mechanics properties, high fracture toughness, high damage tolerance, lower moisture absorption,

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resistance to hot. CF/PEEK composites have the potential to greatly reduce the costs associated with composites manufacture[3], and have been broadly used in the aerospace structures, machinery devices and medical equipments.

CF/PEEK composites can be manufactured by extruding, plastic injection, molding process and Automate Tow Placement (ATP) process [4-6]. Because PEEK molecular structure is very rigid, processing temperature of chopped CF/PEEK compotes are higher, raw materials and molding equipments are specially designed and offered. For example, chopped CF/PEEK granular materials and its structures, prepared by VICTREX Company, need special hot-temperature plastics extruders and injection molding machines the costs is relative higher. In this paper, chopped CF/PEEK premixed by electromagnetic effect mixing equipments, and then, chopped CF/PEEK composites prepared by compression molding technology. This method is highly effective, convenient for mass production, and products with one-timely molded. Finally, the chemical composition, thermo physical and compressive property of chopped CF/PEEK composites had been investigated.

2. EXPERIMENTAL SECTION

2.1 Materials and preparation of samples

The PEEK powders were supplied by JiLin University Super Engineering Plastics Research Co., Ltd (Changchun, China). The density is 1.32g/cm^3 and the granularity is 20μm. its glass transition temperature T_g, the melting point T_m and the decomposition temperature are 143℃, 334℃, and 590℃, respectively. The reinforced fibers are T700SC-12K carbon fiber supplied by Toray Company in Japan.: its tensile strength, tensile modulus, and linear density are 4900MPa, 230GPa, and 800tex,respectively. The carbon fibers were cut and chopped fiber average length is 1.5mm.

2.2 Chopped CF/PEEK premix and preparation of samples

The epoxy-based sizing on the surface of continuous carbon fiber was treated by mixed acid oxidation with ultrasonic concussion, and then the carbon fibers were cut to chopped fiber with length 1.5mm. Firstly, the chopped carbon fibers and PEEK powders were put into electromagnetic effect mixing equipment by 5%, 10%, 15%, and 20% (CF mass fraction), as shown in Fig. 1. Secondly, the strong magnetic particles with an aspect ration (4-6) and a volume of the electromagnetic field (4-6%) were charged into the premixing device. Next, the magnetic induction strength and the premixing time were set as 0.08-0.12 Tesla and 270-380s respectively. The components were mixed uniformly by means of anisometric strong magnetic particles. Finally, the magnetic particles were removed by a magnetic separator and the prepared chopped CF/PEEK premix was get.

The cylindrical samples processing of chopped CF/PEEK composites: Firstly, the produced premixes were added into the cylindrical cavity of the pressing molds, carrying out cold pressing at an applied pressure of 40MPa and holding time of 10min. Secondly, removing the pressure and rising the processing temperature to 380℃, and then pressuring 40MPa and holding time of 10min. Finally, the sample in the molds were cooled to the room temperature in the atmosphere and demoulded. The samples were obtained with a diameter of 10mm and a height of 12 mm.

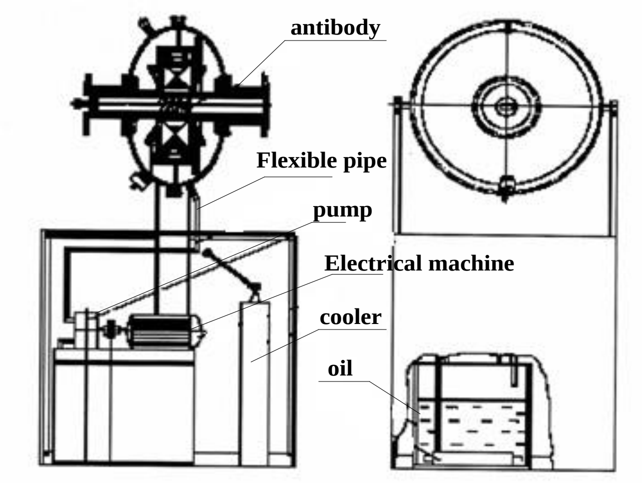


Figure 1: Electromagnetic effect mixing device for chopped CF/PEEK premix

2.3 Performance characterization and Testing

2.3.1 Infrared spectrometry analysis

Infrared spectrometry (IR) analyses were conducted on VERTEX70 infrared spectrometric analyzer, Germany BRUKER Company. Samples of approximately 1mg were taken from cylindrical specimen, grinded into powder, and then placed in the spectrometer with 150mg KBr. The test results were obtained after scanning the samples 16 times.

2.3.2 Thermogravimetric analysis

Thermogravimetric tests for virgin PEEK and chopped CF/PEEK composites were performed with NETZSCH thermogrametric analyzer, model TG 209 F3, Germany NETZSCH Company. Samples of approximately 12mg were heated from room temperature to 800℃ at a heating rate of 5℃/min under a nitrogen gas flow rate of 20ml/min.

2.3.3 Coefficients of thermal expansion measurement

For virgin PEEK and chopped CF/PEEK cylindrical samples, linear coefficient of thermal expansion tests were carried out on DIL 402C thermal expansion apparatus, Germany NETZSCH Company. The samples were continuously heated from room temperature to 360℃ at a rate of 5℃/min under a nitrogen at nitrogen atmosphere.

2.3.4 Specific heat, heat conductivity and thermal diffusion coefficient

Standard specific heat, heat conductivity and thermal diffusion coefficient techniques were used to investigate thermal physical properties of virgin PEEK and chopped CF/PEEK composites. The samples are φ12.7±0.4mm, and 2-3mm high. The tests were run at a heating rate of 5℃/min from room temperature to 280℃ by use of LFA457 Micro Flash, Germany NETZSCH Company.

2.3.5 Scanning electron microscope

The fracture surfaces of PEEK and chopped CF/PEEK composites samples were examined using a scanning electron microscope (JSM-6460LV, Japan JEOL Company).

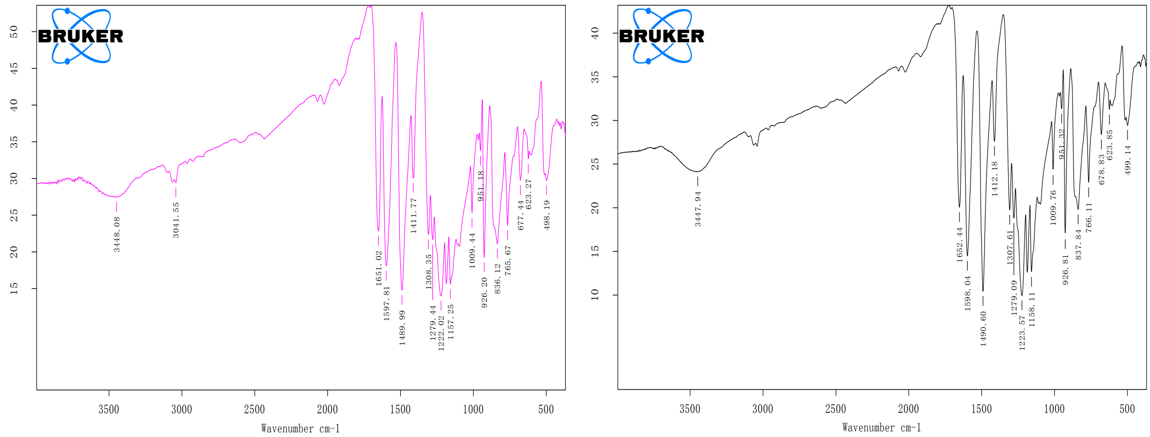
2.3.6 Compressive property

For virgin PEEK and chopped CF/PEEK composites, compress tests were carried out on Instron 4505 type material test system with strain gauge type extensometer at 22℃ and 50% relative humidity. The tests were run at compressing rate of 2mm/min in accordance with the GB/T2569-1995 standard.

3. RESULTS AND DISCUSSION

3.1 Infrared spectrometry analysis

Figure.2 showed the virgin PEEK and chopped CF/PEEK composites IR bonds. The main groups of PEEK molecules are benzene, ketone and aromatic aether bond. Table 1 showed PEEK main characteristic bonds varying with CF mass fraction. Wherein, the extension vibration bond of $C=O$ is 1651.02 cm^{-1}, the plane vibration bond and asymmetric extension vibration bond of $\mathrm{Ar}-O-Ar$ are 1507.81cm^{-1} and 1222.02cm^{-1}, respectively. The plane vibration bond of $Ar-C=O-Ar$ is 1308.36cm^{-1}. 836.12cm^{-1} is the characteristic peak of benzene ring p-substitution.



（a）Virgin PEEK sample （b）Chopped CF/PEEK sample（10wt% CF）

Figure 2: Infrared spectroscopy of virgin PEEK and chopped CF/PEEK samples

Characteristic bond (cm^{-1})	Chopped CF mass fraction (%)				
	0	5	10	15	20
$\nu_{str.}(C=O)$	1651.02	1651.17	1652.44	1652.16	1651.06
$\delta_{def.}(Ar-CO-Ar)$	1308.36	1307.61	1308.22	1307.76	1307.75
$\nu_{as.}(Ar-O-Ar)$	1222.02	1222.81	1223.57	1222.54	1223.18
$\delta_{def.}(Ar-O-Ar)$	1597.81	1597.86	1598.04	1597.67	1597.84
Ar p-substitution	836.12	836.84	837.84	836.47	837.20

Table 1: Characteristic bond for virgin PEEK and chopped CF/PEEK samples

After adding chopped CF fibers, the main characteristic bonds changed a little, the peaks shapes and positions are very approximate. It can be concluded that the structure of PEEK remain stable during the high temperature molding process and no oxidation occurred when PEEK used as the resin matrix.

3.2 Thermo gravimetric Analysis

TGA curves of virgin PEEK and chopped CF/PEEK are presented in Figure 3. It could be seen that the shapes of degradation curves were not different apparently between virgin PEEK and chopped CF/PEEK. T_5, T_{10}, and T_{20} were defined as the temperatures at 5%, 10%, and 20% mass loss, respectively. $T_{v\max}$ is the temperature at which the mass loss fastest, $T_{exothermic}$ is the temperature at which the exothermic peak corresponds to the depolymerization, which are given in Table 2. Under N_2 gas atmosphere, whether it is PEEK or chopped CF/PEEK composites, their heat resistances were good, the initial degrading temperature were all above 545℃. Virgin PEEK began to degrade slowly at around 548℃, and the $T_{exothermic}$ was 574℃. After adding chopped CF fibers, the heat resistance was improved and T_5 of chopped CF/PEEK samples containing 10% (mass fraction) CF fibers was 553℃， higher than that of virgin PEEK by 5℃. However, $T_{exothermic}$ of the chopped CF/PEEK samples decreased a little compared to virgin PEEK.

Chopped CF mass fraction, %	T_5	T_{10}	T_{20}	$T_{v\max}$	$T_{exothermic}$
0	548	560	570	548.9	574
5	545	558	571	548.3	572
10	553	564	577	549.5	574
15	548	560	576	545.9	572
20	546	558	575	541.4	569

Table 2: TGA data of virgin PEEK and chopped CF/PEEK samples (℃)

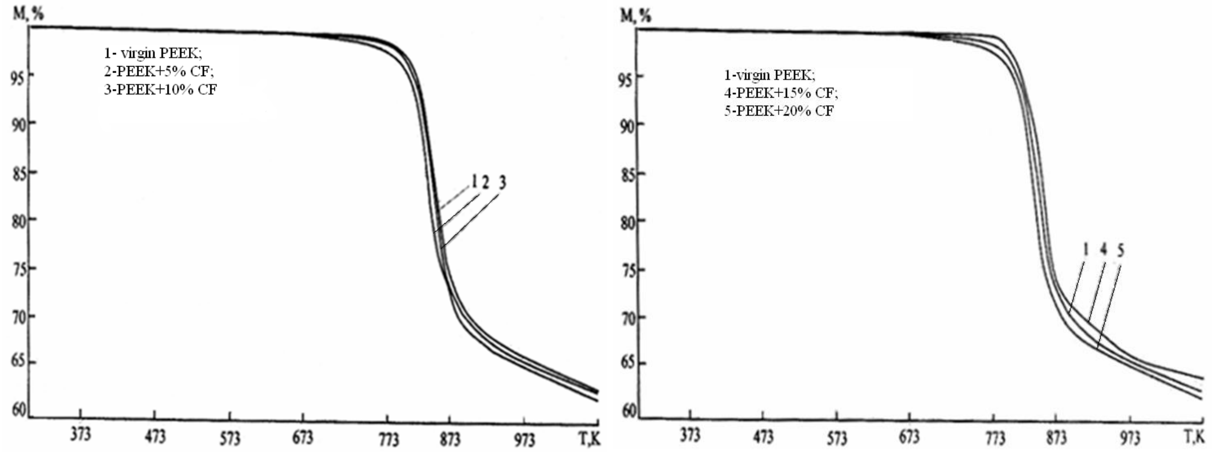


Figure 3: TGA curves of virgin PEEK(1) and CF/PEEK with chopped fibers mass fraction of 5%(2), 10%(3), 15%(4), 20%(5)

3.3 Coefficient of thermal expansion

The linear coefficient of thermal expansion (CTE) is a quantitative characterization of composite expansion properties, which is an important designing index of the composite structure. The smaller CTE give an advantage of stability during the preparation or using process in high temperature environments. The CTE of chopped CF/PEEK composites with different mass content was given in Figure 4. One can see that the CTE remained stable in two temperature stages: (1): First, in the range of -150-140℃，its value is (5-8) $\times 10^{-5}$/K, mainly occurred with the axial linear-elasticity expansion; (2) Second, in the range of 170-260℃, the CTE is (2-5) $\times 10^{-4}$/K, indicating that the chopped CF/PEEK composites still have good dimensional stability in the approximate 250℃. However, in the temperature range of 140-170℃, it is interesting to note that the CTE of chopped CF/PEEK composites rose slightly as ascending temperature, which exceeded PEEK glass transition temperature 143℃. Fig. 4 also showed us that the CTE of chopped CF/PEEK composites decreased slightly as enhancing chopped CF mass fraction, the smallest when chopped CF mass fraction is 20% in this paper.

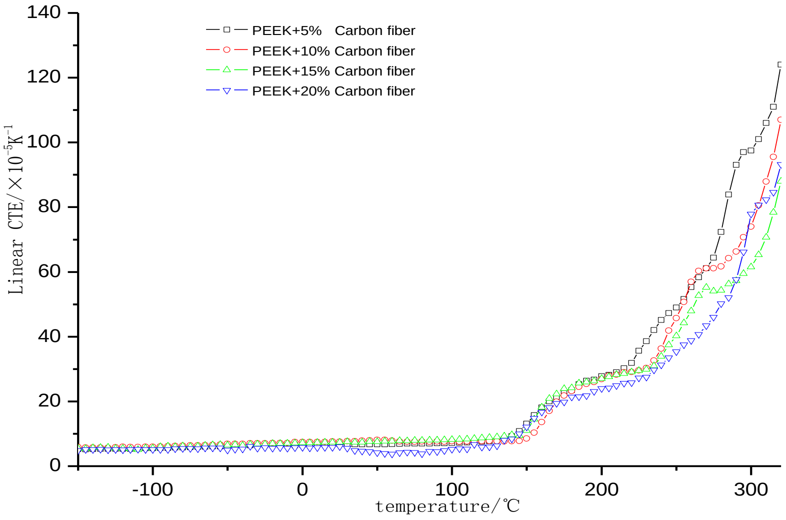
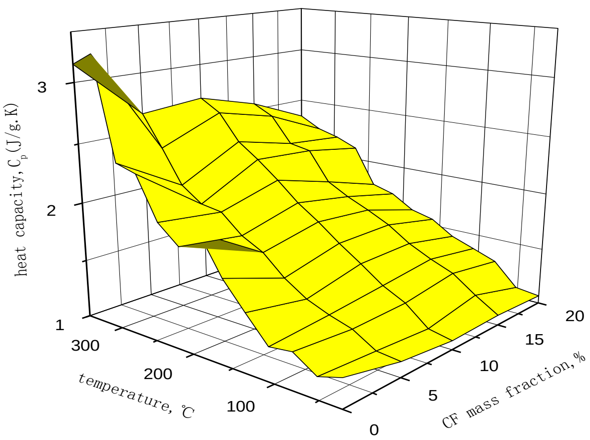


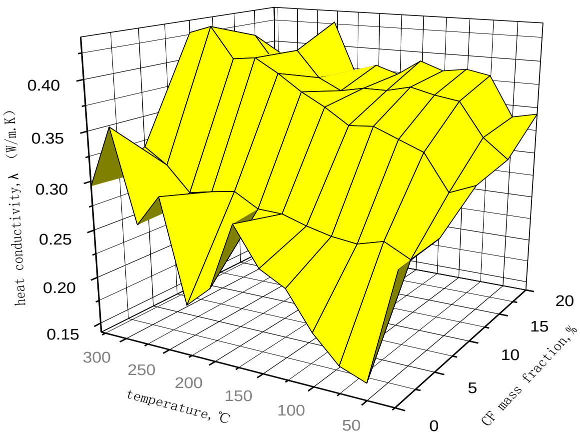
Figure.4: CTE of chopped CF/PEEK composites

3.4 Specific heat capacity C_p, thermal conductivity α, and thermal diffusion coefficient λ

C_p, α, λ curves of virgin PEEK and chopped CF/PEEK composites virus temperature and CF mass fraction were presented in Fig.5(a)-(c). It could be seen that the C_p changed trends were approximately same between virgin PEEK and chopped CF/PEEK composites, which linearly increased with temperature up to 275℃. It could be explained that the segmental motion ability of PEEK's macromolecular dynamic lattice was strengthened. However, the C_p changed sharply from 300℃ to 330℃, due to that the materials physical state changed from glass state to plastic state. In addition, the C_p of PEEK decreases with the addition of chopped CF fibers, which is due to that macromolecular reordering played an important role in two kinds of competition (polymer structure loosening and carbon fiber-PEEK interfacial polymer macromolecular reordering).



（a）



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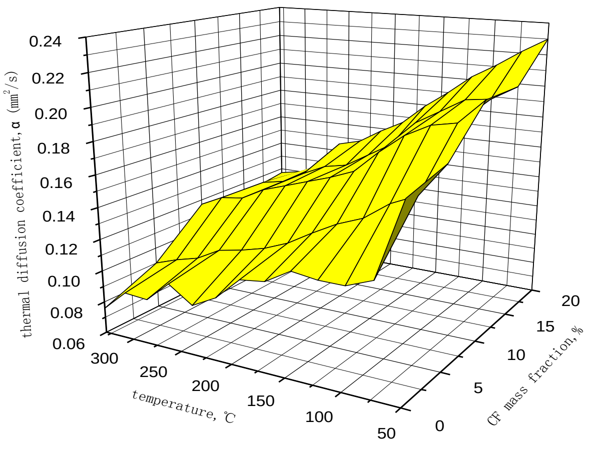


（c）

Figure 5: C_p (a), α (b), λ (c)~t, wt% curves of chopped CF/PEEK composites

Figure 5 also showed that λ, α of PEEK increased sharply after adding chopped CF. According to the lioyad theory, the molecular weight of the chain lattice can be explained by the addition of various atoms and functional groups. And this firstly leads to the difference of physical chain and the unit thermal resistance which have a corresponding direct effect on λ.

3.5 Compression property

The compression properties of virgin PEEK and chopped CF/PEEK composites were presented in Table 3. The effect of the chopped CF mass fraction on the compression property was showed in Figure 6. The data told us that the density of chopped CF/PEEK composites increased with rising CF mass fraction. With chopped CF fibers increased, the compressive property fist increased and then felled, the compressive strength and compressive modulus were 303MPa and 3.69GPa respectively when mass fraction of chopped CF fibers were 10%. While, chopped CF mass fraction exceeded 10%, the compressive strength decreased slightly and compressive modulus more quickly. The change in compress modulus of chopped CF/PEEK composites can be explained by filler reinforcement effect in polymer. After adding chopped CF, the restriction of supermolecular crystal activity happed the surface of PEEK and CF, where PEEK supermolecular generated. The restriction is independent of polymer and filler and can cause modulus changing of materials.

property	chopped CF mass fraction, %				
	0	5	10	15	20
densityρ，g/cm^3	1.312	1.332	1.354	1.376	1.398
$\sigma_{compress}$，MPa	103	211	303	243	263
$\varepsilon_{compress}$，%	4.8	9.4	11.1	13.2	12.6
$E_{compress}$，GPa	2.609	3.530	3.690	3.220	2.890

Table 3: Compression properties of PEEK and chopped CF/PEEK composites

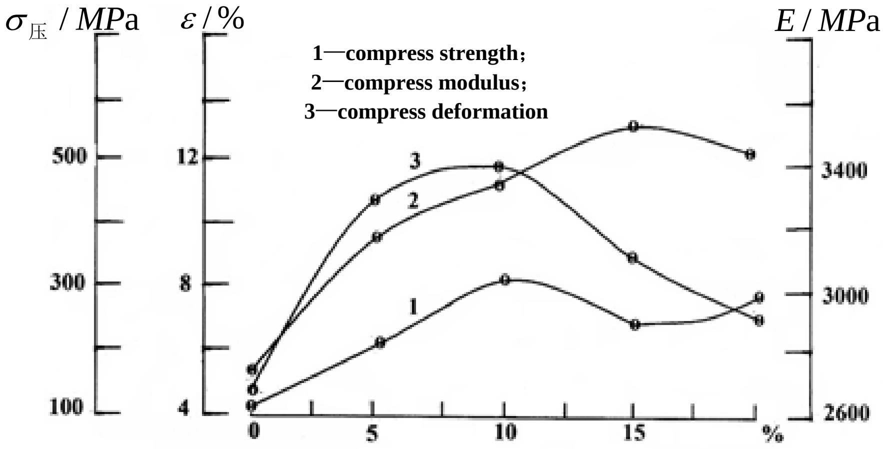


Figure 6: Influences of chopped CF mass fraction on compressive properties

Pressure-deformation curves of chopped CF/PEEK samples were shown in Figure 7. Curve 1, 2, 3 exhibited very short linear elastic deformations stages and were almost nonlinear elastic deformation, this is due to large molecular chains movement not in accordance with Hook's law. However, linear elastic deformation behaved obviously with the rising of CF content, such as curve 4. Then, the parabolic curve can be used to indicate uniform plastic deformation in materials which broke sharply.

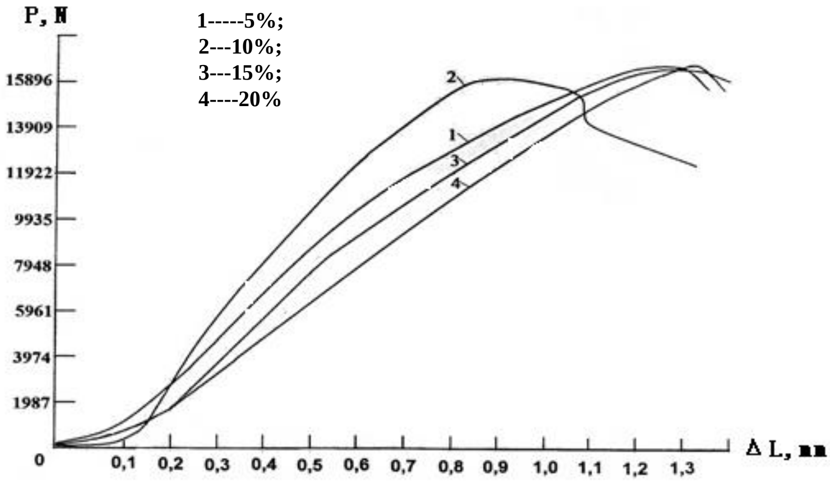


Figure 7: Load-displacement curve under different carbon fiber mass contents

3.6 Compression fracture morphology

In figure 8, fracture macrographs of virgin PEEK and chopped CF/PEEK composites were showed after compress tests. During virgin PEEK samples damaging, crack growth activated the initial destruction, and crack propagated until the final destruction with the increase of compress load. The chopped CF/PEEK samples displayed 45 °shear failure.

Figure 9 showed that SEM micrographs of chopped CF/PEEK composites. The differences of fracture morphology between chopped CF/PEEK composites and PEEK are obvious. SEM also told that chopped CF were evenly dispersed in PEEK matrix by non-axial strong magnetic particles in the rotational electromagnetic fields, and fibers were embedded in the PEEK matrix-cohesive matrix failure. It clearly indicated both good adhesion and insufficient matrix shear strength. According to higher deflection and higher strength at break values (see Table 3), this is indicative of a strong surface bonding between CF fibers and PEEK matrix which can be attributed to the presence of the transcrystalline interphase[]. Chopped CF promoted the formation of supermolecular spherulites and transcrystalline in favor of molecular chain reordering inside polymer resulted in mechanical property changed. Figure 9d showed fracture morphology of CF/PEEK with 15% chopped CF appeared typical spherulites and transcrystalline fractures.

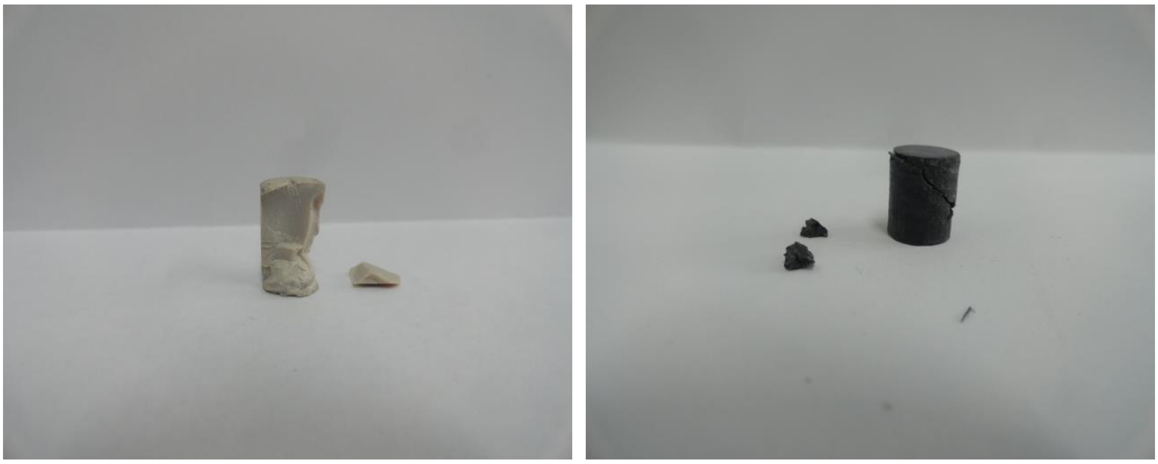
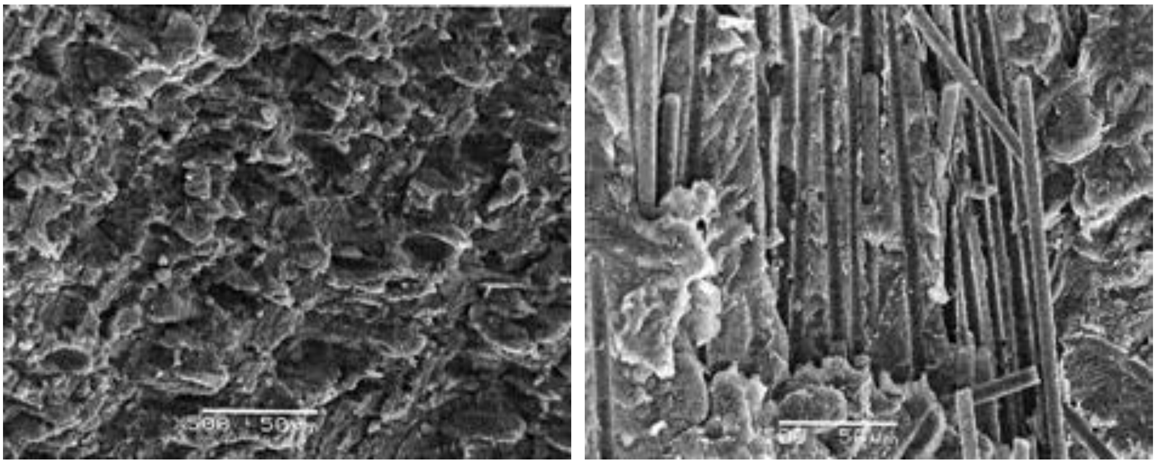
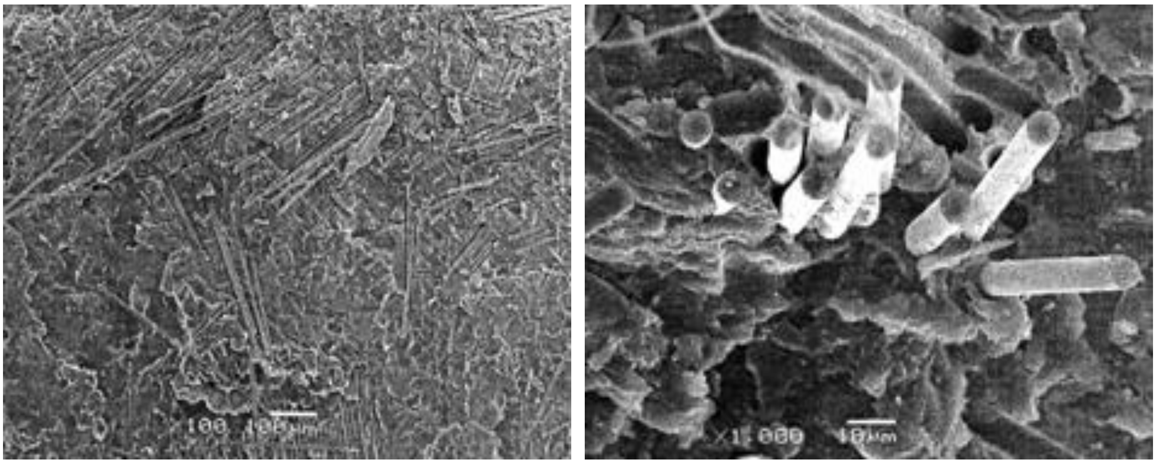


Figure 8: Compression damage graph of PEEK and CF/PEEK cylindrical specimen



（a）　　　　　　　　　　　　　　（b）



（c）　　　　　　　　　　　　　　（d）

Figure 9: SEM morphology of PEEK(a,x500) and chopped CF/PEEK

composites:x500(b),x100(c),x1000(d)

4 CONCLUSIONS

Chopped CF/PEEK composites, as supmarket thermoplastic composites, are widely used in aerospace, precision machinery and other engineering fields. In the paper, chopped CF/PEEK samples were manufactured by electromagnetic induction mixing device and high-temperature mould pressing technology. IR analyses showed the molecular din not oxidize during the molding. PEEK's heat resistance doesn't decrease after adding chopped CF, and could be enhanced by 5℃ when the content of CF is 10%. the CTE of chopped CF/PEEK composites decrease with the rise of chopped CF content, and change a little in the temperature of (-150℃~140℃) and (170℃~260℃)。 From room temperature to 275℃， the Cp of virgin PEEK and chopped CF/PEEK composites both present with approximately linearly increasing, but the Cp of chopped CF/PEEK composites jump in the temperature of (300~330℃) due to PEEK's physical state changing from glass state to plastic state, in addition ,the Cp decreases with enhancing the mass content of chopped CF, but heat conductivity (λ) and thermal diffusion coefficient (α) increase compressive mechanical strength and modulus first increased and then decreased, the maximum value is 303MPa and 3.69GPa with 10% chopped CF mass content, respectively. It could be seem PEEK has good compatibility with chopped CF through the SEM photos, and the fracture images of compression samples appeared typical spherulites and transcrystalline fractures.

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