CARBON-CARBON COMPOSITES WITH TURBOSTRATIC STRUCTURE BASED ON AROMATIC POLYIMIDES

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Introduction

Owing to their unique thermal, mechanical and other properties, carbon-carbon (C/C) composite materials are applied in many technical fields from airspace industry to medicine. They are attractive for tribotechnical applications also.

Polyimides (PIs) can be used for obtaining C/C materials [1] because they exhibit many advantages over traditional binders such as high thermal stability and high coke residue after pyrolysis in the inert atmosphere (up to 70%). That makes it possible to decrease the quantity of re-impregnation stages during the process. Introduction of the mesomorphic pitch into PIs permits the simultanious cheaping of the materials, increase the coke residue and decrease porosity. The effect of mesomorphic pitch on the properties of polyimide binders and physical-mechanical properties of the C/C composite materials has been considered in details in ref [2].

The aim of this work was to study the influence of carbonization and graphitization processes on structure, physical-mechanical and tribological properties of C/C composite materials based on polyimide binders ITA (BTDA/ODA) and PMDA/ODA, which have been developed in the Institute of Macromolecular Compounds of the Russian Academy of Sciences.

Results and discussion

Carbon plastic based on polyimide ITA with 40% (wt.) pitch and polyimide PMDA/ODA with 40% (wt.) pitch exhibited the flextural strength of 970 MPa and 800 MPa, crack resistance of 215 J/m2 and 240 J/m2, thermal stability determined by the glass transition temperature – 360 and 340°C, respectively. According to the data of dynamical mechanical tests, the temperature dependence of mechanical loss modulus was characterised by one transition only. This fact confirmed compartibility PIs with pitch on the molecular level.

Carbon plastics and C/C composites based on ELUR-P01 carbon fibers (Russia) and PI with pitch were studied by nondestructive ultrasonic testing method. These data are listed in Table 1.

Carbon yield for composites based on PMDA/ODA matrix with pitch was more higher than that for ITA with pitch (84% and 73%, respectively).

Table 1

Properties of carbon plastics based on pure PI and PI with 40wt% pitch matrix and C/C composites after carbonization and graphitization.

Sample	Porosity, %	G, GPa	E, GPa
Carbon plastic after curing at 300ºC/1h and 350ºC/5 h, air			
ITA+pitch	5,85	4,83	126.0
PMDA/ODA +pitch	-	2,59	101,1
After carbonization at 1000ºC/1h, nitrogen			
ITA+pitch	15,75	6,203	140,0
PMDA/ODA +pitch	27,23	3,481	114,9
After graphitization at 2200ºC, argon			
ITA+pitch	16.34	5,36	203,5
PMDA/ODA +pitch	28.19	2,71	149,4

G - shear modulus, E - tensile modulus.

It is known that structure and final properties of C/C composite materials are formed during carbonization and graphitization process and determined both of carbon fibers and matrix. Wide-angle X-ray analysis was carried out for three sample types: carbon plastics after curing at 300°C/1h and postcuring at 350°C/5h, carbonized composites (at 1000 °C/1h in nitrogen) and graphitized composites (at 2200° C/1h in argon). Difractogramms from the above mentioned samples were obtained in two directions: 1 - fibers in composite are in the vertical position (perpendicular to the X-ray beam direction); 2 - fibers in composite are in the horizontal position (parallel to X-ray beam direction).

The diffractogramms of the carbon plastics and the carbonized samples in the direction 1 exhibited broad reflection with spacing d = 3.5Å due to X-rays diffraction from [002] plane of carbon fibers. The diffractogramms of carbon plastic and carbonized C/C composites which were obtained in the second position exhibited galo with d = 4.1 Å (because of the matrix) and reflection with d = 2.1 Å (X-ray diffraction from the plane [100] of carbon fibers). This proved that carbon fibers in initial and carbonized samples exhibited the turbostratic packing of the hexagonal layers [1] and binder was in the amorphous state.

After graphitization of C/C samples based on ITA and PMDA/ODA, the diffractogramms obtained in the first position exhibited more narrow and intensive reflection with d = 3.5 Å. This indicates that further improvement of carbon fibers structure (graphitization) took place. The diffractogramms of samples after graphitization taken in the second position also shown strong and more narrow reflection (d = 2.1 Å) with the respect to the initial and **c**arbonized states.

A particular feature of diffractogramms from graphitized samples based on the ITA and PMDA/ODA matrix taken in the second position was the appearance of reflection with d = 3.5 Å (weak for ITA and strong for PMDA/ODA samples). These reflections were absent on diffractogramms of the initial and carbonized samples. Hence, binders after graphitization revealed the turbostratic structure. The average dimentions of odered regions (crystallites) determined by the Sherrer's method [4] were approximately 20 Å for initial (carbon plastic) and carbonized samples. Those for graphitized samples based on ITA matrix were 25-30 Å, and for graphitized matrix based on PMDA/ODA matrix were 30-40 Å.

WAXD data are in a good agreement with mechanical properties of C/C composite (see Table 1). The tensile modulus increased during heat treatment due to the improvement of carbon fibers structure. Shear elastic modulus decreased after graphitization of the C/C composite due to transformation of binders structure to the turbostratic carbon structure.

Tribological properties of C/C composites increased during heat treatment also: friction coefficient decreased from 0.4 to 0.2. Graphitization provided stable behavior of C/C composites (fig. 1) during experiment under load up to 1000H: temperature of tribocontact did not exceeded 270ºC, which was lower than the glass transition temperature of carbon plastics.

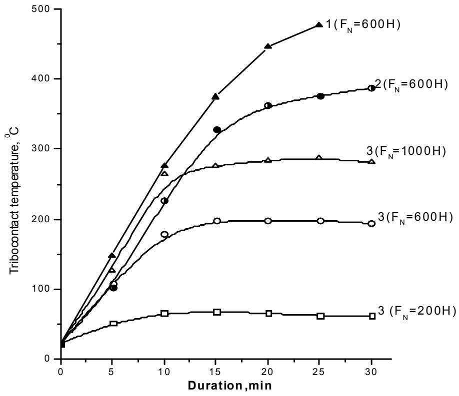

Fig. 1. Tribocontact temperature dependence on duration of experiment at different loads in tribocontact: 1 – carbon plastic, 2 – C/C composite after carbonization, 3 – C/C composite after graphitization.

Conclusions

1. Polyimides ITA and PMDA/ODA with addition of mesomorphic pitch are perspective binders for C/C composite materials with high cox residue (up to 84%) and high mechanical properties.
2. Origin of the turbostratic carbon structure in ITA and PMDA/ODA binders in C/C composites after graphitization at 2200°C was found by WAXD method for the first time.
3. Tribological investigation of developed C/C composites confirmed rather high wear resistance and low friction coefficient, which increased during carbonization and graphitization.

References

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