CARBON-CARBON FILMS AND COMPOSITES BASED ON POLYIMIDES: PROCESSING AND PROPERTIES

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ABSTRACT
Film-forming polyimides were synthesized by transacylation of diacetylic derivatives of aromatic diamines (IDA) by bis-phtalic anhydrides of tetracarboxylic acids. Mechanical and calorimetric properties of these films were investigated. The microporosity texture parameters of C-C films obtained by the IDA method were measured. The possibility to obtain C-P and C-C composites based on this type of polyimides was shown.

KEYWORDS: Polyimides, polyimides films, carbon plastics, carbon films, carbon-carbon composites, mechanical properties, microporous texture parameters

1. INTRODUCTION

Polyimides (PI) are widely used in different fields and particularly in the production of electronic devices as thermally stable polymers (Inagaki , 2000). The most current PI synthesis is a two-stage synthesis with use of aromatic diamine and dianhydride of aromatic tetracarboxylic acids in amide solvents (Bessonov et al., 1987).

This method makes it possible to obtain films with high mechanical properties. However, not all polyimides obtained by this method can be processed into a matrix of the composite materials.

PI can also been synthesized by a single-stage method from dianhydrides and acylated diamines in the melt (IDA method). This method allows the preparation of thermally stable thermosetting binders for composites but these binders are brittle and composites based on them have low interlaminar fracture toughness (Goykhman et al., 1997). It has been shown (Svezlichnyi et al., 2000) that choosing special conditions ductile thermoplastic PI can be obtained by IDA-method. This PI exhibits both film-forming properties and high crack-resistance when they are used as the matrix of composites materials.

PI is very attractive as precursors for carbon-carbon (C-C) composites. Previously it was shown (Yudin et al., 2000) that PI BZF-DADFE (ITA) could

be used as precursors for C-C composites. The mechanical properties of this kind of C-C composites increased with adding to PI matrix 40% of pitch. However it is more effective to use cheaper and commercial available monomers such as DFO-DADFE. Thermal stability of these PI is rather high and preparation regime of C-P is not so complex. In this work PI DFO-DADFE was chosen as precursors for C-C composites.

The possibility to obtain carbon films after heat treatment of polyimides films at high temperature was shown in (Inagaki, 2000). The structure of carbon films (crystallinity and orientation of hexagonal layers) depends on the initial molecular structures of organic precursor.

For carbon films the pores parameters, which are formed during pyrolysis and decomposition of precursor are very important because it represents important textural component of natural and synthetic materials where it plays an essential role in their inner structure and contributes to formation of physical properties. The solid phase forms together with the micro voids a self-contained physical system, which was called „microporous phase" (Weishauptová and Medek, 2002).

In this work PI films were synthesized by using two different methods and then carbonized. The mechanical and calorimetric properties of these films

were studied. The investigation of microporosity of "green" PI films and films after carbonization was carried out.

Carbon plastics (C-P) were obtained on the basis of PI (DFO-DADFE) binder synthesized by the IDA method. Their dynamical-mechanical properties and crack-resistance were studied. The carbon plastics were carbonized. The mechanical properties of these carbon-carbon (C-C) composites were compared with those based on ITA binders studied previously (Yudin et al., 2000).

2. EXPERIMENTAL

2.1. PREPARATION OF PI PRECURSORS

The most current method of aromatic PI preparation is the two-stage synthesis. In the first stage a soluble prepolymer is obtained from which films, fibers, and coating are formed. This reaction stage consists in diamine acylation by dianhydride of tetracarboxylic acid in a polar solvent to give polyamic acid. The second stage is the dehydrocyclization of PI by chemical or a thermal procedure (Method 1). In our work we used a thermal procedure.

Method 1 (traditional method)
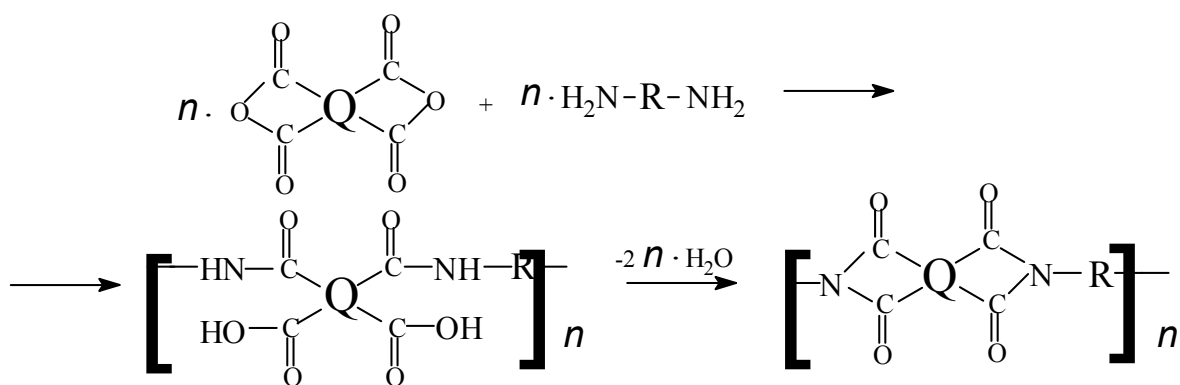
Method 2 (IDA method)
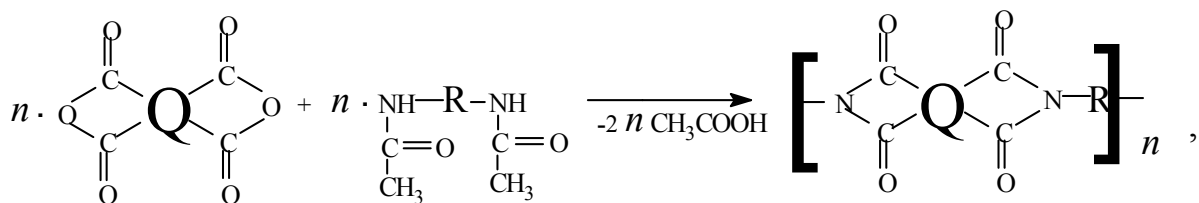
where Q is radical of dianhydride of aromatic tetracarboxylic acid and R is radical of aromatic diamines.

As a rule, according to this scheme, PI films are obtained for subsequent carbonization and graphitization (Inagaki , 2000).

PI can be obtained by the transacylation of 1,4-bis(acetoamido) arylenes by dianhydrides of tetracarboxylic acids (Goykhman, et al. 1997, Svezlichnyi et al., 2000). The interaction of acylated derivatives of aromatic diamines with dianhydrides of tetracarboxylic acids in the melt leads to the formation of a polyimide with a PI structure (Method 2).

The proposed polycondensation mechanism gives readily processable film-forming PI binders and can be used for obtaining carbon-carbon composite material with high crack resistance.

Polyimides films were synthesized by using the traditional two stage method and by the IDA method based on the reaction of dianhydrides with acetylated derivatives of diamines in melt.

In this work we used dianhydrides of 3,3',4,4'-diphenyloxidetetracarboxylic acid (DFO), 3,3',4,4'-diphenylbenzophenontetracarboxylic acid (BZF) as Q and diacetyl derivatives of bis(4-acetaminophenyl)ether (DacDADFE) as R as follows:

Q and **R**

(DFO)

Dac(DADFE)

(BZF)
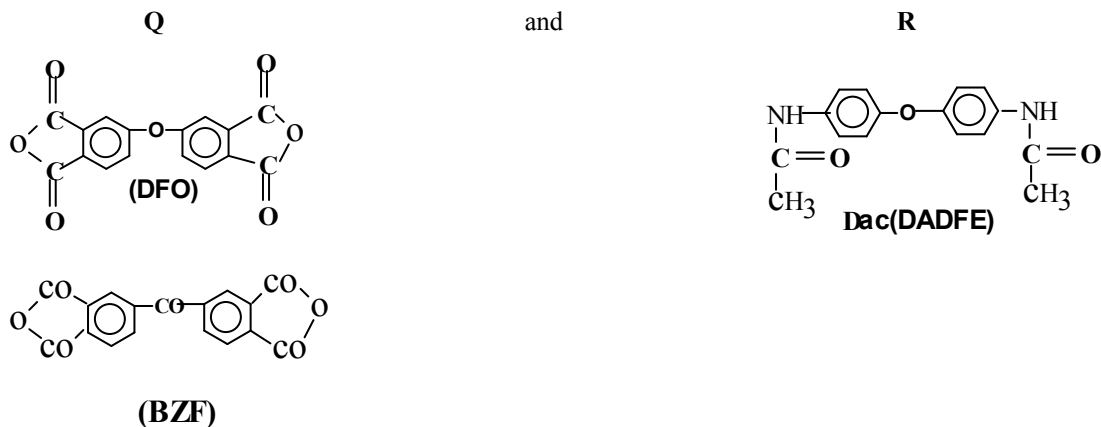
2.2. PREPARATION OF PI FILMS

When the two-stage method was used (method 1) PI films were obtained from solutions of poly(amic acid) in N-methyl-2-pyrrolidone. They were cast on glass plates and dried at 80°C for 12 hours. to remove the solvent and imidized at stepwise temperature rise 100°C, 200°C, 300°C for 1 hour.

To obtain PI films by using diacetyle derivatives of diamine (method 2), corresponding prepolymers were prepared previously by melting equimolar quantities of initial monomers. Film samples were obtained from both the solution and the melt of the prepolymers. For this purpose, the 20% prepolymer solution in N,N-dimethylacetamide was cast on glass plate and the solvent was removed at 100°C for 8 hours. Films were formed from the prepolymer melt on glass supports at 170°C. The films were subjected to further heat treatment at 300°C for 8 hours (with the formation of a crystalline sample) or at 350°C for 1.5 hours (with the formation of an amorphous samples). The films were carbonized at 900°C in the nitrogen atmosphere at a temperature rise of 50°C /h.

2.3. PREPARATION OF CARBON PLASTICS (C-P) AND CARBON-CARBON COMPOSITES (C-C)

The composites were prepared by using ELUR surface-treated PAN-based carbon fibre tows (Russia). Diameter of carbon fiber is 7 μm, a tensile strength is 2.2 GPa and tensile modulus is 200 GPa. The powdered PI obtained by IDA method was deposited onto carbon fibres by electrostatic powder deposition. Prepreg was obtained after impregnating carbon fibres by PI precursor at 250°C using a heated calander. Unidirectional carbon plastics (C-P) were prepared by moulding 24 layers at 0.5 MPa at 350 °C for 1.5 hours.

The carbon plastic composites were carbonized in a nitrogen atmosphere (impurity content <0.002 vol.%) at a heating rate of 50-70°C/h up to 1000°C. The samples were treated at 1000°C for 1 hour.

2.4. METHODS

A strain-controlled dynamic rheometer (ARES, Rheometric Inc.) was used to measure the dynamic shear viscosity of polymers in the cone and plane configuration following standard procedure. The diameter of the plate was 25 mm and the cone angle was 0.1 rad. Nitrogen was used as the heating gas for temperature control. The stacked films or powder in the form of disc were placed between the plates in ARES oven, which was preheated to the required temperature. Testing was done using the oscillation mode with a frequency of 1 rad/s and strain of 1%.

Wide-angle X-ray diffraction (WAXS) measurements were conducted on a diffractometer with a Philips PW-1830 generator. A wavelength of 1.54 nm was generated from a copper K_α source with graphite as the monochromator. Samples were scanned through in the angular range of 10-40°.

Differential scanning calorimetry (DSC) was performed using DSM-2M calorimeter (Russia) on 5 – 10 mg of samples with a heating rate of 10°C/min.

The sorption measurement was performed gravimetrically with a highly sensitive apparatus (IGA 002 HIDEN). This apparatus allows isotherms and the corresponding kinetics of adsorption and desorption to be determined for individual pressure steps (Benham and Ross, 1989). With the samples in grain size 1–2 mm the adsorption and desorption branches of the CO_2 isotherms at the temperature of 298 K within a pressure range from 0 to 1000 mbar were measured. The samples used were outgased until they reached a constant weight, at a pressure of $< 10^{-6}$ Pa at 333 K. The isotherms were evaluated according to Dubinin´s theory of volume filling. Dubinin´s and Medek´s equations (Dubinin, 1958, Medek, 1977) were applied to the calculation of the basic texture parameters, i.e. the volume of micropores V_{micro}, characteristic energy E, the surface area S_{micro} and micropores distribution represented by the most frequent radius $r_{mode.}$

The shear storage G' and loss G'' modulus of the same samples were determined by using a custombuilt torsion pendulum developed in the Institute of Macromolecular Compounds (Yudin et al., 1997). The torsion pendulum experiments were performed under the conditions of free-damping oscillation at a frequency range of 0.4-1 Hz.

Interlaminar fracture toughness G_{IC} of unidirectional composites was measured by the double counterlever beam method on a 1958U-10 (Russia) testing machine at a load speed of 10 mm/min.

The open porosity of the composites was obtained from density d_{H2O} values determined by the water penetration method according to the ASTM C-20 standard. Water was chosen as a penetrating liquid in order to enable detection even of the smallest pores unaccessible to commonly used kerosene or butanol.

The microstructure of the C-P and C-C composites was studied using a NICON optical microscope equipped with a Hitachi HV-C20 TV camera and a digital image grabbing system.

3. RESULTS AND DISCUSSION

Both crystalline and amorphous films may be based on PI obtained by the IDA method from the prepolymer by the melt or the solution technology. Rheologic and structural features of prepolymer have been previously investigated. Fig.1 shows the time dependences of IDA prepolymer melt viscosity after heating at 300°C for 30-60 min. The rheologic behavior of melt was studied at 270°C. The data indicate the viscosity of DFO-DADFE prepolymer melts is very low and increases slightly for an hour. This behavior shows that this prepolymer can be easily processed into film. Additional temperature treatment is necessary for processing this prepolymer type into the matrix of a composite material.

A drastic increase in BZF-DADFE prepolymer with time is due to crystallization processes. During 30 minutes viscosity increases by three orders of magnitude. This limits the processing time of this prepolymer into matrix of the composite material.

The existence of a crystalline phase is proved also by the X-ray diffraction results (Fig.2). Sample 2 shows a series of the distinctive crystallinity peaks. X-ray diffraction of prepolymer DFO-DADFE (sample 1) is characterized by amorphous galo, which confirms that prepolymer DFO-DADFE is amorphous.

On the basis of IDA prepolymers 40 μm thick films were prepared. Their physico-mechanical characteristics were compared with those of their analogues obtained by the two-stage method. As can be seen from Table 1, the PI films in the amorphous state obtained by the IDA method can be compared to films obtained by the traditional two-stage method as regards Young's modulus E and tensile strength σ_p. But the elongation at break ε_p of the latter is much higher. The glass transition temperature T_g is also depended on method of obtaining of films.

Table 2 gives data on melting temperatures T_m and enthalpies of melting ΔH_m for crystalline films obtained by the IDA method. It was shown that the crystallinity for films based on BZF-DADFE is much higher than for DFO-DADFE. Crystalline films were brittle and the mechanical properties can not be measured.
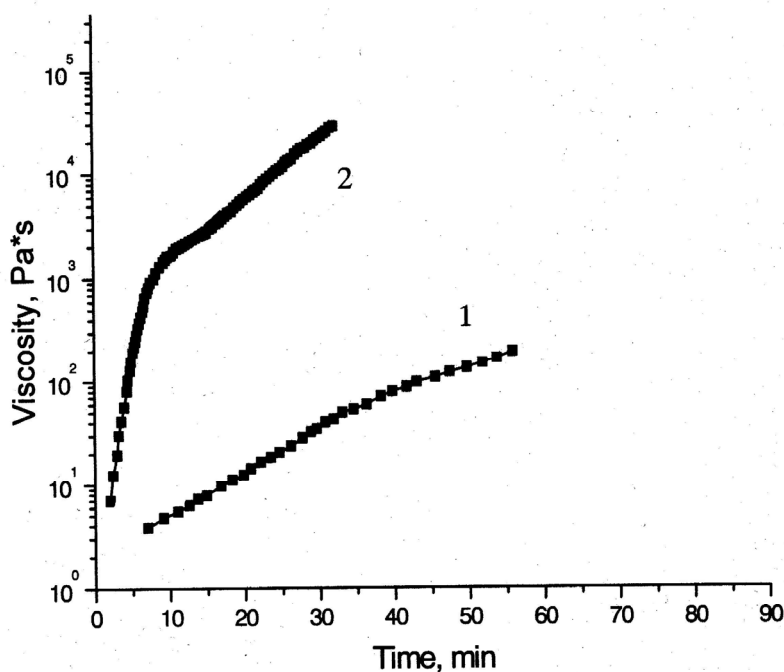

Fig. 1 Time dependence of viscosity at 270°C for IDA prepolymers based on: (1) DFO-DADFE, (2) BZF-DADFE.
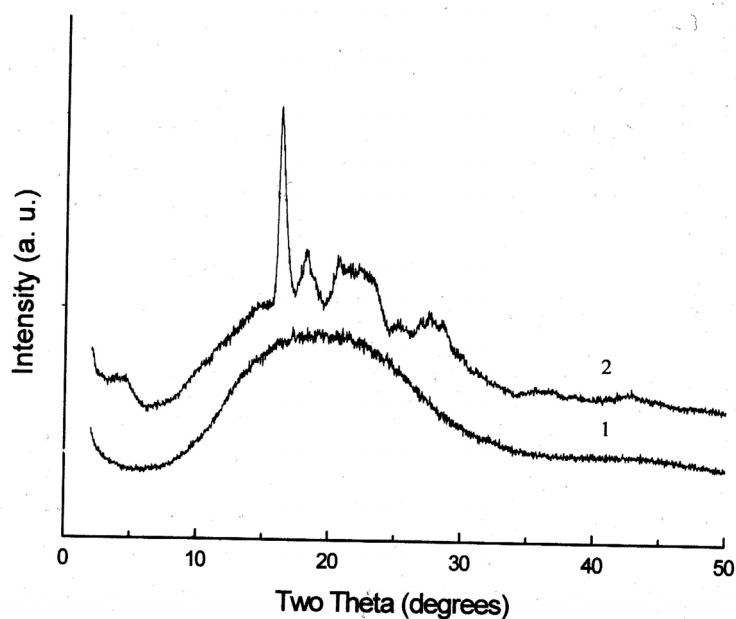
Fig. 2   Wide angle X-ray scattering patterns for IDA type prepolymers after curing
at 270°C for 1 hour: (1) DFO-DADFE, (2) BZF-DADFE.

Table 1 Film properties of PI, made from DFO, and BZF dianhydrides and acetylated derivatives of diamine
(DADFE) in amorphous state

Method	Film (PI)	E (GPa)	σ_p (MPa)	ε_p (%)	T_g (°C)
2	DFO-DADFE	2.48	152	35	297
2	BZF-DADFE	3.86	132	6	324
1	DFO-DADFE	3.2	170	90	270
1	BZF-DADFE	3.2	150	15	280

Table 2 Film properties of PI, made from DFO, and BZF dianhydrides and acetylated derivatives of diamine
(DADFE) in crystalline state

Method	Film (PI)	T_m (°C)	ΔH_m (J g^{-1})
2	DFO-DADFE	345	7.7
2	BZF-DADFE	408	74.0

It is seem, that method 2 (IDA) made it possible to obtain the films both in amorphous and crystalline state and the films obtained by method IDA in amorphous state were flexible, but the mechanical properties of amorphous analog obtained by two-stage-method were higher.

The appearance of crystallinity can be explained in the framework of the polycondensation mechanism. Since the reaction takes place in the melt at 300-330 °C, low molecular weight imide-containing products formed at the beginning of the reaction (dimers and oligomers) exhibit high mobility. Therefore, they can implement their tendency to the ordering of mutual arrangements, which is thermodynamically advantageous for these compounds. These structures consisting of imide-containing oligomer fragments should be characterized by higher melting temperature than these at which the melt of the initial materials is formed, 270 °C. Therefore, they do not melt and are not decomposed existing in the form of stable aggregates. The formation of these aggregates is probably the initial stage of polymer crystallization. In this case a

drastic decrease in the mobility of chains contained in these aggregates hinders further chain propagation and leads to its stop.

An important parameter of both carbon films and carbon-carbon composite materials is their porosity. The pores structure is formed in all stages of the technological process and their amount and size distribution is influenced by the thermodynamic conditions of this process. Technological conditions influence above all the formation of large pores, whereas the formation of the smallest pores with radii < 2 nm (micropores) is the natural property of synthetic polymeric materials after heat treatment. Formation of group of larger pores was detected by determination of open porosity (Table 5) decreasing the mechanical properties of PI films and carbon-carbon composite. The micropores affect the formation of electrical and physical properties of carbon film (Inagaki , 2000).

With respect to different technological conditions leading to the formation of crystalline and amor-phous PI films the character and textural parameters of their microporous structure were studied by means of CO_2 sorption. The differences in sorption behavior of crystalline and amorphous films are shown in Figure 3.

The amorphous samples are characterized by overrun of desorption branch, which make evident the difficulty in removing CO_2 molecules from the disarranged amorphous structure. On the contrary, in case of crystalline sample the course of adsorption /desorption process is reversible. At amorphous samples where the sorption occurs by a slowly proceeding diffusion process also a low values of the rate constant was observed, whereas at crystalline sample the values of rate constant are significantly higher as it corresponds to reversible course of adsorption/desorption.

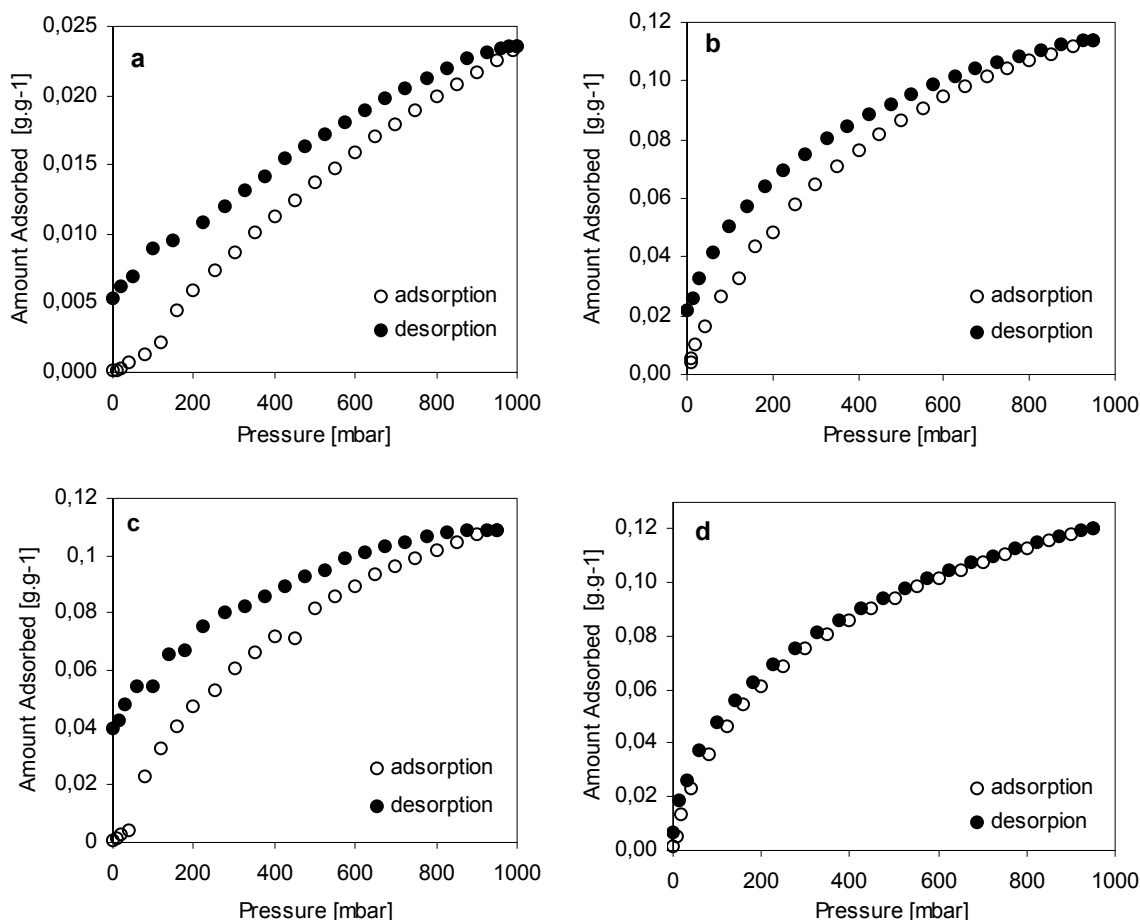The textural parameters of micropores structure of PI films are shown in Table 3.

Fig. 3 CO_2 sorption isotherm at 25°C on a) green sample DFO-DADFE, b) amorphous sample DFO-DADFE after carbonization, c) amorphous sample BZF-DADFE after carbonization, d) crystalline sample DFO-DADFE after carbonization

Table 3 Textural parameters of micropores structure of PI's films

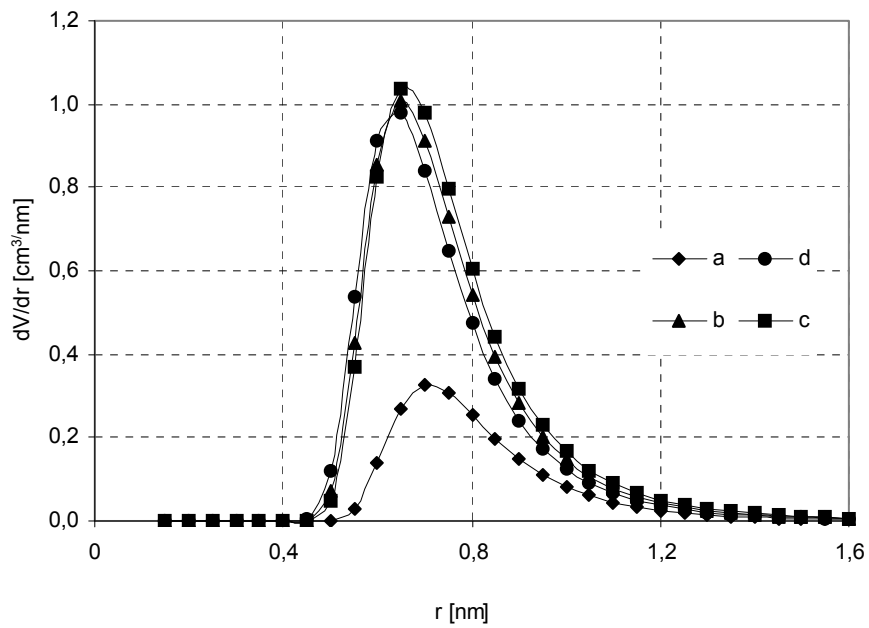| Sample	V_{micro} (cm^3g^{-1})	E $(kJ.mol^{-1})$	S_{micro} (m^2g^{-1})	r_{mode} (nm)
DFO-DADFE amorphous, green	0.1059	8.16	270	0.70
DFO-DADFE amorphous, carbonized	0.3007	10.56	836	0.65
DFO-DADFE crystalline, carbonized	0.2879	11.32	819	0.65
BZF-DADFE amorphous, carbonized	0.3169	10.12	866	0.65

Fig. 4 Distribution curves of micropores of a) green sample DFO-DADFE, b) amorphous sample DFO-DADFE after carbonization, c) amorphous sample BZF-DADFE after carbonization, d) crystalline sample DFO-DADFEafter carbonization

Table 4 Properties of C-P composites based on IDA

Sample	Polymer	Technological regime	G_{1c} (Jm^{-2})	T_m (^oC)	ΔH_{melt} (Jg^{-1})	T_g (^oC)	$G^{'}_{25^oC}$ (Pa)
1	DFO-DADFE	$350^0C/1.5$ h $+350^0C/5h$ after curing	420	380	22	290	$4.8 \ 10^9$
2	DFO-DADFE	$350^0C/1.5h$, $+350^0C/5h$ $+390^0C/15min$ after curing	650	-	-	280	$7.1 \ 10^8$

From the values of the micropores volume V_{micro} and the surface area S_{micro} the influence of carbonization process on the structure arrangement is evident. These parameters are in the case of green sample significantly lower. It may be supposed that during the carbonization the atoms of hydrogen and oxygen are degraded and the number of voids, especially of micropores increases.

Mode of radii r_{mode} shows the change of pores distribution (Fig.4) and the characteristic energy E indicating the most probable value of the adsorption potential. The increasing value of E and the decreasing value of r_{mode} are caused by the refinement of the microporous structure, which is realized during the heat treatment of DFO-DADFE green sample. The r_{mode} values of samples in amorphous and crystalline state are identical, however the E values show a difference between those both states. A different intensity of the adsorption field is characteristic for these materials.

The proposed PI-IDA film-forming binders can be used to obtain carbon composites with high crack resistance. Depending on the conditions of preparation, films and carbon plastics based on DFO-DADFE PI (IDA) can be either crystalline or amorphous.

Table 4 gives melting temperature T_m and enthalpy ΔH_{melt} of crystalline binders in the carbon plastic, glass transition temperature T_g, shear modulus G' and interlaminar fracture toughness G_{lc} both for amorphous and crystalline carbon plastic. It is noteworthy that the melting enthalpy of pure PI (Table 2) is low as compared to that of the same polymer in composite

materials. This is probably due to carbon fiber affect on the matrix structure because the film can be crystalline only when subjected to additional heating. Carbon plastic based on crystalline matrix DFO-DADFE has the interlaminar fracture toughness 420 J/m^2 (sample 1). Carbon plastic sample annealing at 380°C makes the binder amorphous. In this case crack resistance of the sample increases to 650 J/m^2 and shear modulus decreases because the binder loses its crystalline state (sample 2). It should be noted that the increase of interlaminar fracture toughness owing to disappear of crystallinity (by heating sample higher than the melting temperatures) is observed only after short-term heating (not more than 10 min.)

Fig.5 shows temperature dependences of shear elastic modulus G' and mechanical losses modulus G'' for carbon plastics based on DFO-DADFE matrix in the crystalline (curves 1',1") and the amorphous state (curves 3',3"). Amorphization of the samples was obtained by heating at the temperature higher than melting temperature (at 390°C). The shear elastic modulus considerably decreases after amorphization and the thermal stability of the composite also decreases from 380° to 300°C. Thermal stability was determined as the temperature of maximum G''. Temperature dependence of G' and G'' for carbon plastic without additional temperature treatment is done with curves 2' and 2". It is seen that shear modulus is dramatically dropped at 230°C and then increased. It may be connected with the growth of crystallinity with the increasing of experimental temperature.
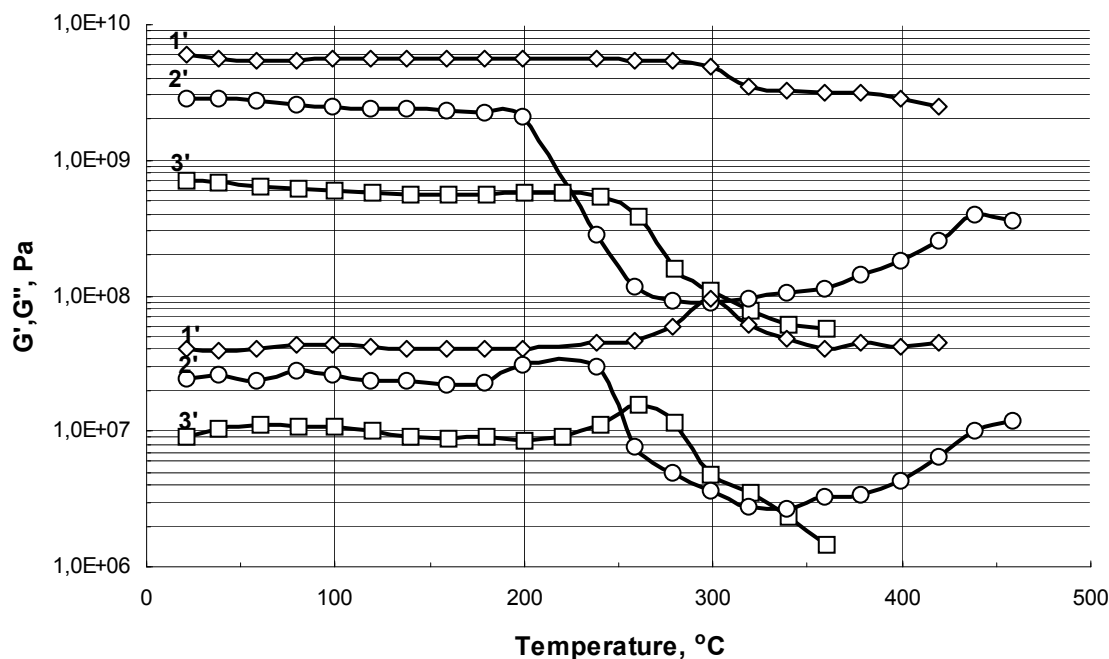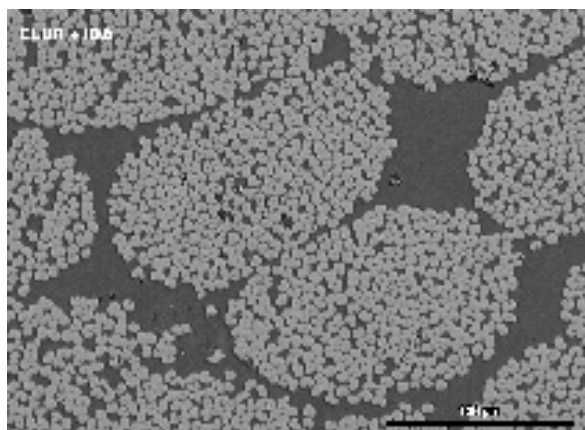

Fig. 5 Temperature dependence of the shear storage G' and loss modulus G'' of carbon plastic in crystalline state (1',1"), after curing without additional temperature treatment (2',2") and after amorphization (3',3").

Table 5 Properties of C-P composites based on ITA and IDA matrix before and after carbonization (at 1000°C/1h, nitrogen)

Method	Sample	Porosity (%)	d_{H2O} (gcm^{-3})	G (GPa)	E (GPa)
Before carbonization					
IDA	C-P after curing at 350°C/1.5h, air; post-curing 350°C/3h	6.82	1.44	5.52	144.02
ITA	C-P after curing at 300°C/1h,air post-curing 350°C/5h	11.30	1.32	3.52	114.5
ITA	C-P +pitch 40% curing at 300°C/1h,air post-curing 350°C/5h	5.85	1.42	4.79	126.0
After carbonization					
IDA	C-C	25.47	1.31	-	148.5
ITA	C-C	28.75	1.23	2.84	127.9
ITA	C-C +pitch	20.79	1.36	4.91	140.0

Investigation of open porosity and density d_{H2O} have shown that these parameters for C-P samples based on PI (DFO-DADFE), obtained by the IDA method, are greatly lower (6.82%) than those for C-P based on ITA binder (11.30%) and are comparable with the latter when mesomorphic pitch was added (5.85%). Data on porosity and density for C-P in the initial and carbonized states are listed in Table 5. After carbonization at 1000°C in nitrogen the open porosity grew significantly up to 25.47 %, but was still lower than for C-C composites based on ITA (28.75 %). Young's modulus for C-C based on IDA was much higher than for C-C based on IDA. It may be supposed that open porosity can be decreased using more slowly heating rate during carbonization. Other possible improvement of C-C properties is to add pitch to PI (IDA).

The microscopic investigation (Fig.6) shows rather good quality of C-P sample with high compa-

tibility between fibers and matrix. The mean diameter of pores is about 13 μm, the maximum value of pores diameter is about 70 μm.

4. CONCLUSION

1. Polyimides were synthesized by transacylation of diacetylic derivatives of aromatic diamines (IDA) by bis-phtalic anhydrides of tetracarboxylic acids. This method makes it possible to obtain film-forming polyimides (σ = 120-152 MPa, ε =10-35%, E =2.3-3.8 GPa), which can be used as a binder for crack-resistance composite (G_{1c} = 650 J/m^2). The films obtained by IDA method can be in amorphous and crystalline states.

2. The sorption analysis has shown by means of standard textural parameters of microporous structure the development of microporosity during the carbonization process. The different mechanism of desorption indicates the differences between the crystallic and amorphous structure.

3. Polymer DADFE-DFO (IDA) may be used as precursor for C-C composites. Their open porosity and density are lower than that for C-C based on pure ITA and comparable with C-C based on ITA with pitch. Mechanical properties of C-P and C-C based on PI IDA are higher than for ITA and ITA with pitch.

Fig. 6 Optical microphotograph of the polished surface of a C-P composite based on IDA.

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