

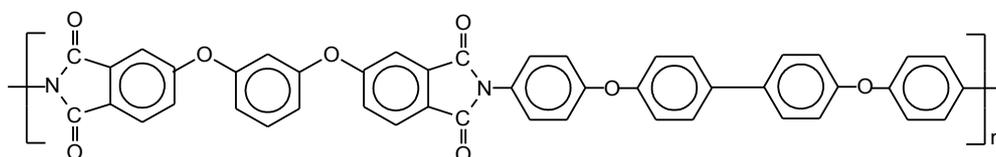
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## ATOMIC FORCE MICROSCOPY AND STRUCTURAL INVESTIGATIONS OF R-BAPB-TYPE POLYIMIDE FILMS MODIFIED BY CARBON NANOFIBERS

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In our previous works [1–5], the crystallization behavior of a new semicrystalline polyimide (PI) based on 1,3-bis-(3,3',4,4'-dicarboxyphenoxy)benzene (R) and 4,4'-bis-(4-aminophenoxy)biphenyl (BAPB) with the chemical structure:



was investigated. It was found that variation of processing conditions, addition of low molecular weight bisimides, varying of the molecular weight of the PI, and addition of carbon fibres [4] or carbon nanotubes [5] significantly influenced crystalline morphology of this polymer and its ability to crystallize from melt.

In this paper, we report, as a next step in these investigations, an influence of uniaxial drawing and carbon nanofiber modification of these PI films on their supermolecular structure and crystallinity

### Experimental

The R-BAPB PI films of 30–40  $\mu\text{m}$  thickness were prepared as follows: poly(amic acid) (PAA) was obtained by polycondensation of 1,3-bis(3,3',4,4'-dicarboxyphenoxy)benzene (R) and 4,4'-bis-(4-aminophenoxy)biphenyl (BAPB) in a 25 wt. % solution of N-methyl-2-pyrrolidone (NMP) at 25  $^{\circ}\text{C}$  and subsequent drying at 80  $^{\circ}\text{C}$  for 20 h. PI films were prepared from the PAA by casting on soda lime glass plates and oven curing under air. Imidization was achieved by heating the films in air oven for 15 min at 50  $^{\circ}\text{C}$  and 100  $^{\circ}\text{C}$ , then rapid heating till 280  $^{\circ}\text{C}$  and slow heating during 2 h till 300  $^{\circ}\text{C}$ . A dilute Vapor Grown Carbon Fibers (VGCF) suspension in NMP (0.1 vol. %) was prepared by homogenization for 10 min in ultrasonic bath (40 kHz). The BAPB diamine was added into the VGCF suspension. The VGCF and diamine mixture was stirred for 20 min before adding dianhydride and phthalic anhydride (PA). 30–40  $\mu\text{m}$  thick VGCF/PI composite films were prepared with 1–5 vol.% from VGCF-PAA solution as for the neat PI films.

Uniaxial drawing was performed using laboratory set-up [4] at 250  $^{\circ}\text{C}$  up to draw ratio  $\lambda = 5.5$ . PI film samples filled with 3 wt. % VGCF) were prepared according to the procedure described in [3]. Atomic force microscopy (AFM), wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) techniques were used for the structural characteriza-

tion of films.

## Results and discussions

DSC curves obtained for PI and nanocomposite samples under study display three distinctive features: the glass transition with  $T_g$  in the region of 203–209 °C; exotherm in the region of about 250–300 °C, and melting endothermic peaks with the maxima at  $T_m = 313$ –329 °C.  $T_g$  as well as the narrow glass transition range  $\Delta T_g = 8 \pm 2$  °C are rather stable for these films and practically do not change at the second scan. This allowed to suppose that amorphous phase in this type of PI remains quasi-independent, at the first approximation, from the crystalline phase. Therefore, R-BAPB PI may likely be considered as two-phase system, unlike more complicated dynamic/structural behavior of typical semi-crystalline polymers. An exotherm may be associated with not only crystallization of PI films but also with energy release as a consequence of improvement of molecular packing in amorphous phase. The value of melting endotherm depended on several factors including the drawing temperature and modification by CNF. Some of DSC data are listed in Table 1.

DSC data show that the introduction of nanofibers increases the enthalpy of melting of PI films more effectively than uniaxial drawing. Contrarily, enthalpies of exotherms after uniaxial drawing of R-BAPB and VGCF/R-BAPB PI films are notably higher than for undrawn samples. WAXS data also confirm that uniaxial drawing of PI films at temperature higher than the glass transition temperature (above 215 °C) increases the crystallinity degree up to 20 %, at draw ratio  $\lambda > 4$ . According to WAXS data, introduction of carbon nanofibers (3 wt. %) leads to increasing the degree of crystallinity from 5 to 10 % for undrawn VGCF/R-BAPB sample.

Table 1

DSC data obtained for R-BAPB and VGCF/ R-BAPB PI films in the range of 25–360 °C, at the heating rate of 10 °C/min

Sample	Scan	$T_g, ^\circ\text{C}$	$\Delta C_p,$ J/(g·K)	Exotherm Temp. region, °C	$\Delta H_{\text{exo}},$ J/g	Endotherm	
						$T_m, ^\circ\text{C}$	$\Delta H_m, \text{J/g}$
1. Undrawn PI film	I	205				322	8
2. Drawn PI film, $\lambda=5.5$	I	208	0.23	250–300	0	323	9.7
	II	208	0.23	–	–	–	–
3. Undrawn PI film, with 3 % VGCF	I	209	0.16	270–300	2.7	323	13.1
	II	209	0.25	–	–	–	–
4. Drawn PI film, with 3 % VGCF, $\lambda=5.5$	I	205	0.13	230–300	21.3	313 329	29 3.8
	II	203	0.30	–	–	–	–
5. GVCF/PI film drawn, at 250 °C 3 wt% GVCF, ( $\lambda = 5.5$ ) and annealed at 280 °C/3h	I	212	0.07	–	–	323	43

Simultaneously, the enthalpy of melting attains 13 J/g (Table 1). Uniaxial drawing of VGCF/R-BAPB PI films and subsequent annealing at 270 °C led to growth of the degree of crystallinity up to 45 % (WAXS data) and 57 % (DSC data). Moreover, the latter drawn nanocomposite films became after heating up to 300 °C almost totally crystalline. It should be also noted that the crystallites orientation in PI films has not been detected by WAXS after drawing as we usually observed for the other semi-crystalline PIs [6].

DSC curves of VGCF/R-BAPB PI films display, after their uniaxial drawing at 250°C, two endotherms, at  $T_{m1} = 313$  °C and  $T_{m2} = 329$  °C, which may correspond to melting of two different types of crystallites (Fig. 1, *b*), while undrawn PI films is characterized by the only one endotherms at 322°C (Fig. 1, *a*).

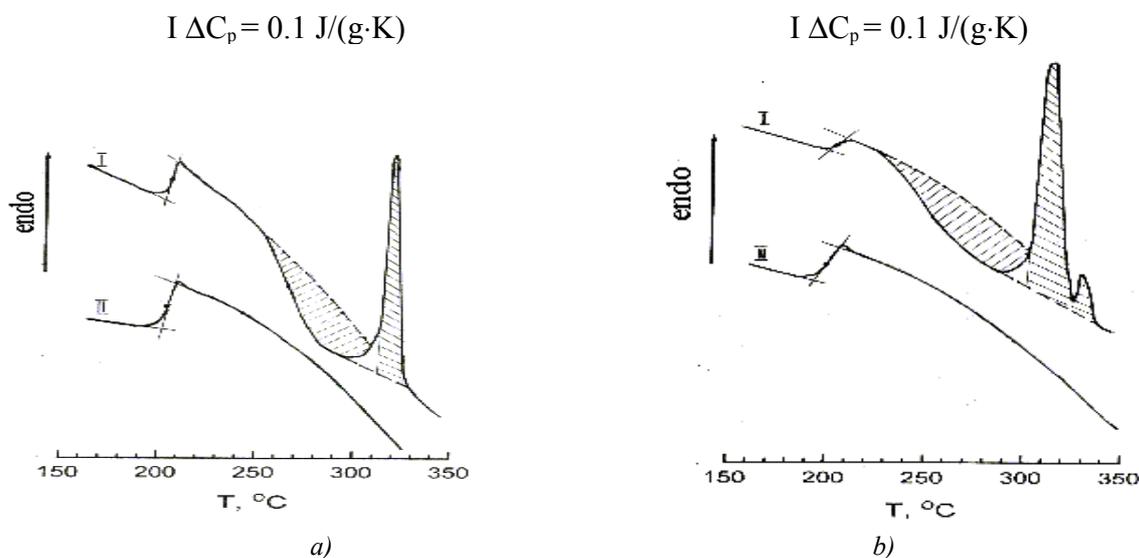


Fig. 1. DSC thermograms of : *a*) R-BAPB at 10 °C/min scan rate for PI film, after amorphisation at 360 °C/10 min and then crystallized at 280 °/2h; *b*) DSC thermograms of VGCF/ R-BAPB (1 wt.% of VGCF) at 10 °C/min scan rate for PI film drawn at 250 °C ( $\lambda = 5.5$ ). I – first scan, II – second scan

This observation is in accordance with AFM data which display two drastically different types of morphology in the drawn R-BAPB PI films filled with 3 wt. % VGCF (Fig. 2, *a*). While the first type has a spherulitic morphology, the second type resembles the shish-kebab structure. It is highly probable that this peculiar morphology is connected with shear stresses during preparation of these filled PI films. Under higher resolution (Fig. 2, *b*), stack of lamellae with a thickness from 60 to 180 nm and two kink bands crossing the film surface (at the angle about 30 °C to one another) are clearly seen. Consequent annealing at 280 °C during 3h leads to appearance of third type of morphology – quasi-lammelar (Fig. 2, *c, d*), which followed by essential increasing of melting enthalpy – up to 43 J/g (table 1, sample 5).

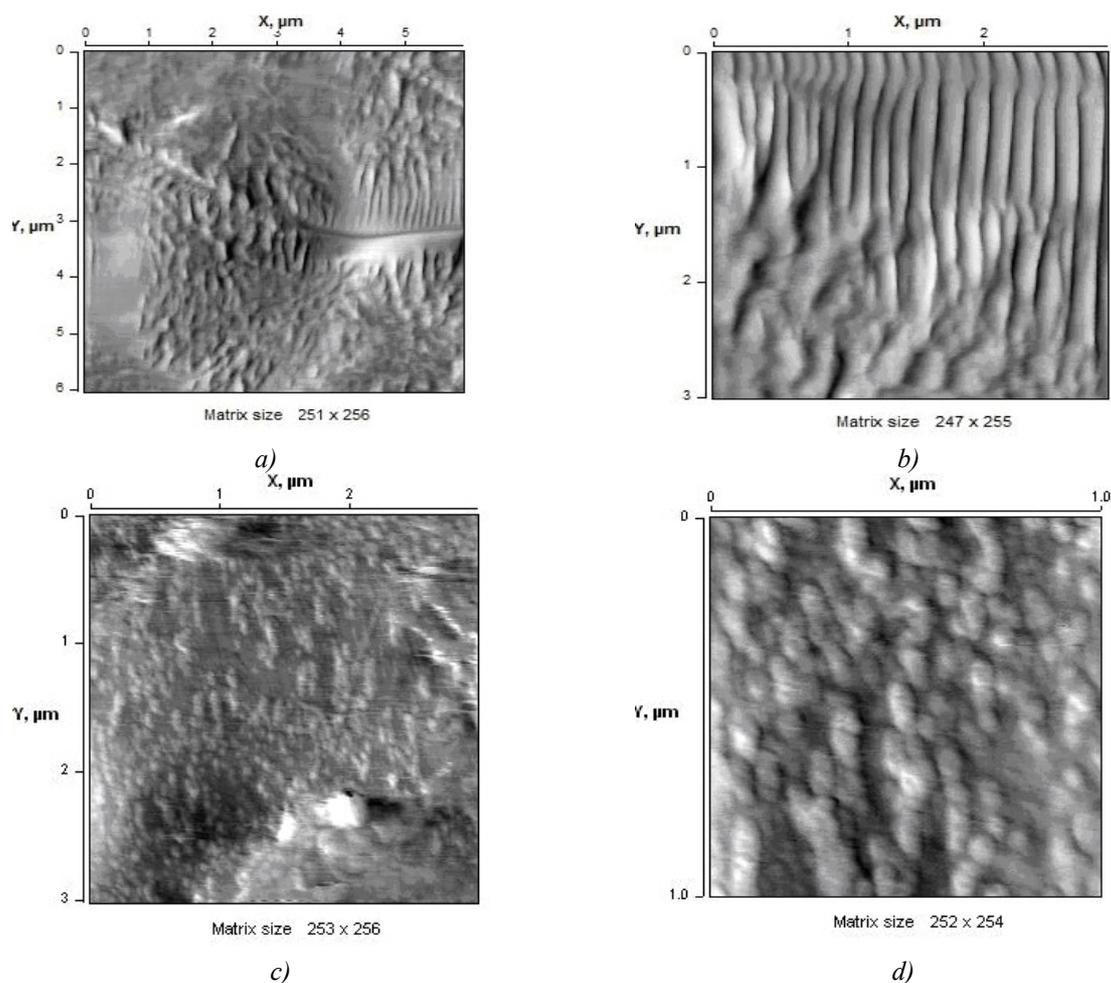


Fig. 2. AFM images of VGCF/R-BAPB PI film surface with 3 wt. % nanofibers,  $\lambda = 5.5$  (a, b); annealed film at 280 °C/3h (c, d)

## Conclusions

1. Influence of uniaxial drawing and embedded nanofiber modification of the PI films on their supramolecular structure was shown by AFM, DSC and WAXS.

2. The presence of two different crystalline morphologies was detected by AFM method. Also, two melting endotherms observed by DSC after drawing of VGCF/PI nanocomposite films confirmed AFM data.

3. Drawing of the VGCF/PI nanocomposite film and subsequent annealing result in failure of the initial spherulitic morphology and formation of the quasi-fibrillar type of morphology.

## References

1. Yudin V.E., Svetlichnyi V.M., Gubanova G.N., Didenko A.I., Sukhanova T.E., Kudryavtsev V.V. // J. Appl. Polym. Sci. 2002. 83. 2873.
2. Sukhanova T.E., Grigoriev A.I., Svetlichnyi V.M., Yudin V.E., Gubanova G.N., Matveeva G.N., Volkov A. Didenko A.L., Kudryavtsev V.V., Ratner S. and Marom G. Polyimides and Other High Temperature Polymers / Ed. by K.L. Mittal. 2007. Vol. 4 . Pp. 47–66.
3. Суханова Т.Е., Вылегжанина М.Э., Новиков Д.В., Кутин А.А. и др. // ВМС. 2008. Т. 50, № 3. С. 467–478.

4. Yudin V.E., Svetlichnyi V.M., Gubanova G.N., Didenko A.I., Sukhanova T.E., Kudryavtsev V.V. Polyimides and Other High Temperature Polymers // K.L. Mittal, Ed; VSP, USA, 2003, Vol. 2, 523.
5. Yudin V.E., Svetlichnyi V.M., Shumakov A.N., Letenko D.G. // Macromol. Rapid. Commun. 2005. 26.
6. Smirnova V.E., Gofman I.V., Gubanova G.N., Yudin V.E., Sukhanova T.E. // Russ. J. Appl. Chem. 2006.