

NANOSTRUCTURE, MORPHOLOGY AND PROPERTIES OF HYDROLYTICALLY STABLE ADAMANTANE-CONTAINING POLYIMIDES AND COPOLYIMIDES

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Introduction

Aromatic polyimides (PIs) have become the most prominent and important class of thermally stable polymers, which are widely used in various technological and industrial applications [1]. They possess the advantageous combination of technical characteristics – excellent thermal and oxidative stability, good mechanical and dielectric properties, non-flammability, self-lubricity and others. But, their major drawback is rather low hydrolytic stability [1]. In order to improve this particular aspect, the chemical modification of PIs by a rigid adamantane (AD) fragments were carried out successfully [2–4]. It has been found that the incorporation of bulky hydrophobic AD groups into the polyimide structure provides high hydrolytic stability of these polymers and low moisture absorption [4].

In this work, three sets of novel AD-containing PIs and coPIs (AD-PIs and AD-coPIs, respectively) with the concentration of AD-containing fragments *n* varied from 0 to 100 mol. % are presented. Comparative WAXD/TEM/AFM structural studies of the AD-PIs and AD-coPIs films are performed. In parallel, their densities, tensile testing, thermal and thermo-mechanical behavior in combination with hydrolytic stability are studied.

Experimental

AD-based poly(amic)acids (AD-PAA) and copoly(amic)acids (AD-coPAA) were synthesized by a conventional two-step method [1] using two types of AD-containing diamines: 1-aminoethyl-3-(4'-aminophenyl)adamantane (AEAPhA) and 1-amino-methyl-3-(4'-aminophenyl)adamantane (AMAPhA), 4,4'-oxydianiline (ODA) and pyromelitic or 3, 4, 3', 4' – tetracarboxydiphenyl oxide dianhydrides (PMDA and ODPDA, respectively) The inherent viscosities of the AD-PAA and AD-coPAA, measured in DMF at 25°C, were in the range of 1.86–4.2 dl/g for the I set, 1.09–4.2 dl/g for the II set and 0.72–1.60 dl/g for the III set, decreasing monotonically as the AD content in the polymer chains increases. The AD-PAA and AD-coPAA films were cast onto glass plates, and then dried at 80°C. The thermal conversion of the films into corresponding PIs/coPIs was carried out by heating up to 300°C. Resulted films, 20–25 μm thick, were transparent and pale yellow in color.

Wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and

atomic-force microscopy (AFM) techniques were used for characterization of the structure and morphology of samples. Mechanical tests were carried out in the uniaxial tension mode and thermomechanical analysis has been performed by heating the film specimens at a rate of 5 deg/min under the action of the extensional stress ~ 0.5 MPa. The hydrolytic stability of the films was determined by studying the variations of the mechanical properties after exposure to a 5 % NaOH solution at 20°C or 20 % NaOH solution at 80°C. The densities of the PI films were estimated by the flotation method in the mixtures of toluene and CCl_4 at 20°C. The thermogravimetric analysis has been performed in the air conditions at the heating rate of 5 deg/min. The temperatures of 1, 5 and 10 % of mass losses (τ_1 , τ_5 , and τ_{10} , respectively) have been estimated.

Results and discussion

The structural characterization was made first by WAXD method with the “as received” and annealed films. The annealing of the samples was carried out at temperatures $\sim 15^\circ\text{C}$ below T_g for each polymer. In the WAXD profiles of all samples of I and II sets two broad reflections (halos) were observed corresponding to $2\theta = 6^\circ$ and 18° , respectively.

Analysis of the d -spacings has shown that as the content of AD fragments increases, both reflections shifts to smaller angles, i.e., the Bragg’s spacing corresponding to the second maximum increases from 5.1 to 5.7 Å (for I and II sets, Fig. 1), from 4.9 to 5.8 (for III set). Another important feature to be considered is that the first reflection at $2\theta = 6^\circ$ becomes narrow and intensive after annealing for homo-PI PMDA-ODA that corresponds to the formation of a smectic-like structure [5]. This reflection broadens and decreases in the intensity while introducing the AEAPhA into polymer chains (up to 50 mol. %), and becomes diffuse in AD-coPIs with 80 mol. % AEAPhA in annealed samples. Contrary, the d -spacing corresponding to the second reflection is practically unaffected by the annealing.

For all three sets, density measurements show the permanent decreasing of the ρ values with the increasing the AD content in coPIs from 1.408 to 1.310 g/cm^3 for I set (Fig. 2), from 1.408 to 1.294 g/cm^3 for II set and from 1.375 to 1.271 g/cm^3 for III set. These variations can be explained by: 1) the loosening of the polymer structure; 2) the incorporation into the polymer chains of the AD fragments with the local density less than that of the unmodified polyimides [6].

The annealing of the samples results in considerable increasing in density for I and II sets of AD-coPIs (Fig. 2). According to WAXD data, this corresponds to the formation of more ordered mesomorphic structure. This fact reflects the tendency to the thermostimulated ordering of the PMDA-based PIs [1]. However, up to 80 mol. % AEAPhA, no changes were seen in the density curve of the III set coPIs after annealing by reason of the higher flexibility of the ODPА-based copolymers.

So, the data above demonstrate the loosening of the film’s molecular packing by the bulky asymmetric AD units. Moreover, polymer chains interactions can be leveled down by the increase of the average interchains distances in AD-coPIs.

The surface structure of AD-coPI films was studied first by TEM, using the gold decoration technique [7]. Based on the cluster lattice model [8] of polymers structure, the correlation radii ξ , the lattice densities ρ_l , and the fractal dimensionalities D of macromolecular clusters on the film surfaces were calculated from the spatial distribution parameters of the decorating gold particles, according to the procedure described in [7].

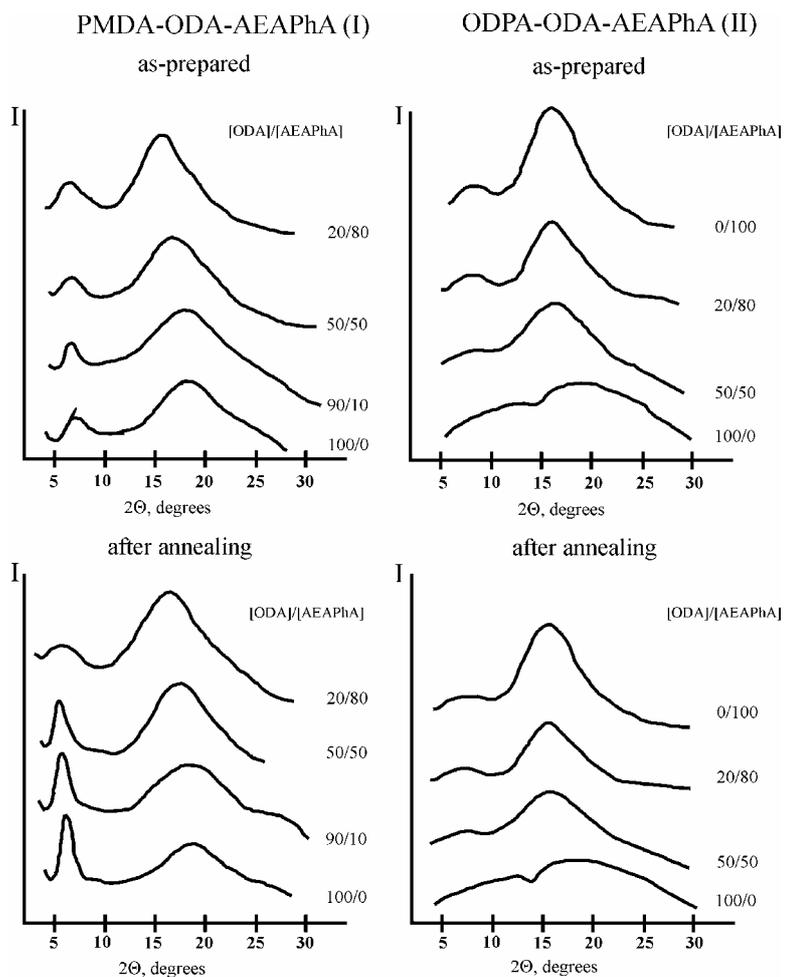


Fig. 1. Wide-angle X-ray diffraction patterns of AD-PIs and AD-coPIs of different compositions

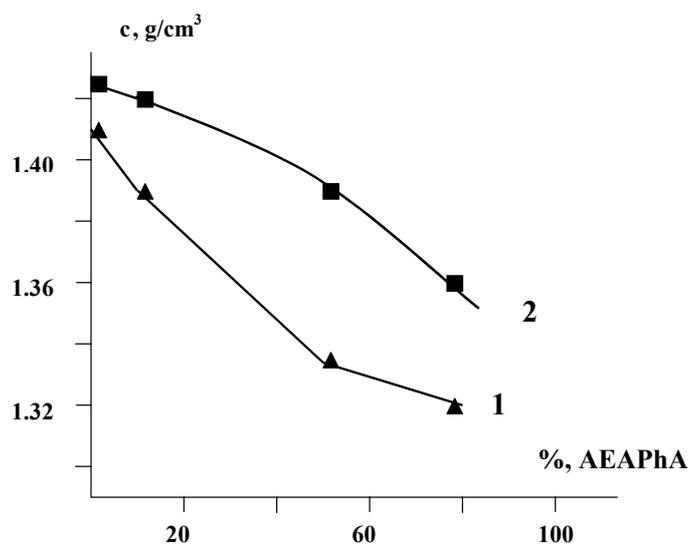


Fig. 2. Density dependence of the PM-DADPhE-AEAPhA on the concentration of AEAPhA: 1- as received, 2- after annealing 30 min at 300° C

It was found that as the AD fragments content in coPI films increases, D increases too in the I and II sets, while ρ_1 and ξ permanently decrease. These results can be explained by the more homogeneous distribution of clusters density on the AD-coPIs surface as compared with the homo-PI PMDA-ODA. At the same time, the formation of the more homogeneous physical network of the continuous cluster on the films surface with increasing of the AD-fragments content was evident from TEM micrographs.

According to the AFM images obtained in the contact mode, surface topography with “light effect” of films of the I and II sets has weak grainy structure (Fig. 3). Comparatively large pores are visible on the surface of the homo-PI PMDA-ODA film (a). The increasing of the AEAPhA concentration from 0 % (a) to 50 mol % (c) and 80 mol % (d) leads to the substantial roughening of the films surface. On the opposite, the films surface of the III set is more flat.

TEM and AFM investigations demonstrate the reduced surface porosity, formation of the more loose clusters and more homogeneous physical network of the continuous cluster as well as roughening of the films surface with increasing of the AD-fragments content.

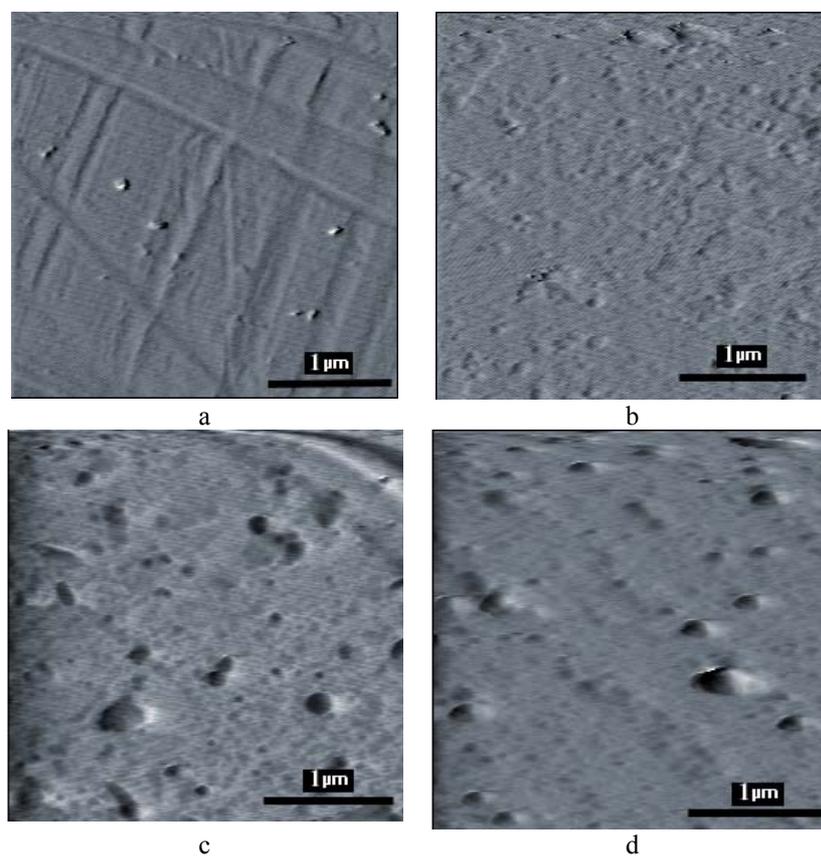


Fig. 3. AFM images of surface topography of the homo-PI PMDA-ODA (a) and AD-coPI (b-d) films of the I set with the AEAPhA content 10 (b), 50 (c) and 80 (d) mol.%. The size of the each image is $3 \times 3 \mu\text{m}^2$, the maximum real height of the islands about 15 nm

Tensile and thermomechanical characteristics of the above polymers are presented in Table 1 and Fig. 4. For I set of AD-PIs, mechanical tests demonstrated the slight in-

creasing of the yield point when the AEAPhA content increased. Also, the incorporation of the AD fragments leads to the depression of the glass transition temperature T_g (from 367 to 330°C). This table also indicates that while the AD fragments content has been varied the Young's modulus was practically constant for this set of AD-coPIs.

Table 1. Tensile and thermomechanical properties of the AD-containing PIs and coPIs

Sample No	AD-containing diamine concentration, mol. %	E, GPa	σ_y , MPa	σ_b , MPa	ϵ_b , %	T_g , °C
I set						
I-1	0	2.98 ± 0.09	103 ± 1	150 ± 2	65 ± 3	367
I-2	10	2.83 ± 0.11	104 ± 2	113 ± 2	31 ± 3	360
I-3	50	2.89 ± 0.09	108 ± 1	108 ± 1	23 ± 2	345
I-4	80	2.97 ± 0.09	117 ± 1	116 ± 1	14 ± 1	330
II set						
II-1	0	3.63 ± 0.11	149 ± 4	235 ± 5	93 ± 4	266
II-2	50	3.35 ± 0.06	133 ± 4	158 ± 1	64 ± 4	271
II-3	80	3.36 ± 0.11	131 ± 1	136 ± 3	60 ± 4	275
II-4	100	3.22 ± 0.05	124 ± 2	124 ± 4	59 ± 3	268
III set						
III-1	0	2.98 ± 0.09	103 ± 1	150 ± 2	65 ± 3	372
III-2	10	2.89 ± 0.08	100 ± 1	145 ± 2	71 ± 2	376
III-3	20	2.84 ± 0.09	89 ± 1	102 ± 2	25 ± 2	372
III-4	50	3.14 ± 0.11	103 ± 2	98 ± 1	16 ± 1	371
III-5	80	3.26 ± 0.10	105	103 ± 1	8.0 ± 0.5	377

E – Young's modulus;

σ_y – yield point;

σ_b – tensile strength

ϵ_b – elongation-at-break

T_g – glass transition temperature.

For the most rigid AD-coPIs of II set, with short aliphatic groups in the AD-containing diamine fragments, we observed the increasing in the Young's modulus from $E = 2.98$ to 3.26 GPa by the AD content increase. For the PIs of III set, more flexible than I and II, we observed the decreasing of both the Young's modulus and yield point. It was interesting to observe, that there was no influence of AD content on the T_g in the AD-coPIs of the II and III sets.

Thus, three different sets of AD-based CoPIs display various kinds of mechanical and thermomechanical behavior depending on the AD-fragments concentration. But, one common feature should be emphasized: for all three sets of the AD-coPIs the elongation at break and

the break stress considerably decreased with the increasing of AD content.

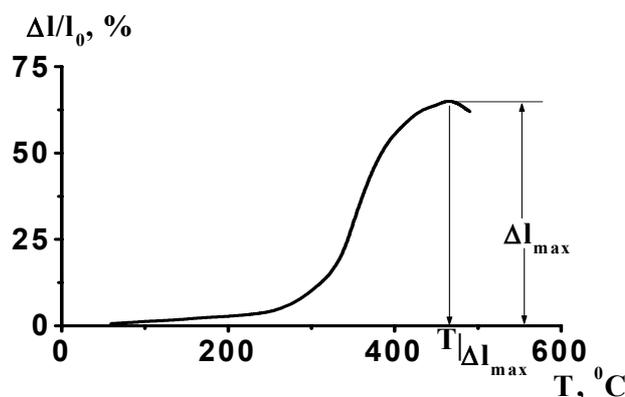


Fig. 4. Typical thermo-mechanical curve of the PM-DADPhE-AEAPhA films

The thermogravimetric results demonstrate the gradual decrease of the thermal stability of the AD-coPI films as the AD units concentration increases. For example, the increase of the AD units content in the diamine fragments in I and II sets from 10 to 80 mol. % leads to the 50-60°C fall of the τ_5 value. The effect may originate in the extremely high thermal stability of unmodified PI films [1] as well as in the presence of aliphatic $-(CH_2)_n-$ groups in the AD-containing diamine units.

The commonly available PI films exhibit moderate hydrolytic stability and absorb water from the atmosphere up to several weight percents. This results, first of all, in the instability of their dielectric characteristics [1].

Our study demonstrates the substantial enhancement of the stability of the stress-strain properties of PI films in the conditions of the long-term alkaline hydrolysis as a result of the incorporation of the AD units into the macromolecules. The most noticeable positive effect has been obtained while the AEAPhA fragments were used. For example, after the 4 days exposition in 5% NaOH solution at 20°C of the films of I set containing 80 mol. % of AEAPhA in diamine fragments residual values of σ_b and ε_b are 90 and 103 % of the initial values, respectively. But, under the same conditions, the coPI film containing 80 mol. % of more rigid diamine AMAPhA has the residual values of σ_b and ε_b of 3 and 6 % only. It should be noted there that the conventional PMDA-ODA film became absolutely destroyed after 2 days of exposition in 5% NaOH solution.

Taking into account the higher hydrolytic stability of the coPIs based on the ODPA dianhydride as compared with that based on the PMDA, the stability toward hydrolysis for the III set of coPIs was determined in a more severe conditions – in 20 % NaOH solution at 80°C. As in the previous case, while the content of AEAPhA units in coPI macromolecules increases, the hydrolytic stability increases too.

A distinctive feature of the AD-coPI films is the increase in their stress-strain properties at the initial stage of the hydrolysis. The explanation of this effect needs the additional experimental studying.

Conclusions

1. Using the AD-containing diamines, tough and flexible AD-coPI films have been produced. These films have tensile strengths of 98–158 MPa and initial moduli of 2.8–3.4 GPa. Increase in AD-concentration results in gradual lowering of the elongation-at-break of films under study.

2. The presence of bulky hydrophobic AD fragments in the polyimide structure leads to copolyimides possessing increased stability toward hydrolysis and low moisture absorption.

3. Increase of the AD-fragments concentration results in decrease of density along with loosening of the polymer structure as evidenced by a monotonous shift of the reflections to smaller angles in the diffractograms of AD-coPIs, suggesting an increase of the average interchain distance.

4. TEM and AFM images demonstrate a reduced porosity and more homogeneous distribution of cluster density on the AD-coPI films surfaces as compared to the homo-PIs.

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