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Polyimides with improved operational by properties*

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Abstract: One of directions of basic researches in the field of chemical process engineerings is making new polymeric materials for electronics and aviation technique distinguished by boosted production characteristics.

The value of aromatic polyimides (PI) as industrial thermally sound polymers is well-known. However alongside with a complex of valuable properties they have also series of shortages: high temperatures and difficulty of reaching of 100% conversion at ring formation polyamic acids (PAA) and their instability in time, low stability to hydrolysis, poor adhesion to line of substratums etc. all this in some cases restricts or makes to impossible application PI in practice.

The complex examinations, spent by us, the solid-phase of thermal cyclyzation PAA and its model junctions have reduced in an establishment of correlation associations between a degree and velocity of ring-formation, thermal stability and reagent resistance, stregth that has allowed to govern process of deriving PI with a necessary level of production characteristics. Use of some components, for example, heterocyclic basic amines-azoles, promotes acceleration and lowering of a temperature band of ring-formation PAA, and also magnification of a degree of ring-formation, that reduces in a considerable raise thermal and chemical resistance, mechanical and dielectric parameters and insulant properties which are not varying at long-lived operation.

The modes of deriving of various materials designed on the basis of industrial PAA of a lacquer consisting in introduction of azoles, plasticizing and adhesion components. It is shown, that the coats obtained from modified polymers, have boosted adhesion, high thermal, mechanical, insulant and other properties maintained in requirements of climatic trials.

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The basic mode of deriving PI is two-steps synthesis, at which first stage will spend polycondensation aromatic diamine with dianhidride tetracarboxilic acid with formation of soluble polyamic acid. At the second stage the response of polyring-formation flows past, as a result of which the usually nonsoluble poly-

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mer different unit of a structure is gained.

As the properties PI in basic are included at a stage ring-formation, theoretically magnification of a degree of ring formation, i.e. the diminution different unit of a structure should reduce in a raise of physico-chemical performances PI.

The complex examinations, spent by us, solid-phase thermal ring-formation PAA and its model junctions have reduced in an establishment of correlation associations between a degree and velocity of ring formation, mechanical hardness, thermal stability and chemical resistanse, that has allowed to govern process of deriving PI with a necessary level of production characteristics. Use of some components, for example, heterocyclic tertiary amines - azoles, promotes acceleration and lowering of a temperature band of ring-formation PAA, and also magnification of a degree of cyclization. The examinations were spent simultaneously by several methods: TGA and DTA, TMA, IR-spectroscopy, X-ray diffraction analysis, gas chromatography et al. The temperatures of a beginning and termination ring-formation, particular various methods, are well compounded among themselves. As it is visible from the Table 1, in case of the components of benzimidazole and imidazole will increase specific reaction rates by 1-2 order, and the values of an activation energy decrease in 1,5-2 times. Thus the ring-formation is terminated at 493-523 K, and without the components at 573 K. The degree of cyclization is incremented on 5%-10 %.

All this positively has an effect on properties of the obtained polymers, first of all magnification of a thermostability PI. The considerable odds in temperatures of a beginning of intensive destruction PI is observed which defined by the begining of losses of a mass and sectional DTA. Besides it is necessary to note, that at PI, obtained without the components, the loss of a mass even prior to the beginning expansion is observed, that is probable, is bound to expansion of defect links. The experimental data and the spent theoretical calculations have shown, that in our requirements of ring formation preferred is amic-acides different unit of a structure, and therefore initial losses of a mass are stipulated possible decarboxilic reaction.

There is a good correspondence between a degree of ring formation and temperature began as thermal destruction in air, and at expansion in inert (argon) to an atmosphere. PI obtained by ring formation PAA at the presence of azoles have major values of coke residue at thermoshock on air.

The estimation of a thermostability by methods TGA and DTA frequently does not give representation about substantial serviceability of polymer. Therefore most reliable representation about heat stability of polymer as future material is given by examinations of a modification both chemical constitution, and physical properties at long-lived heating-in requirements of heat ageing.

In the Table 1 the association of losses of a mass of recordings PI is shown at isothermal heat at 573 K on air from a nature inlet in PAA of the component. An aging of recordings spent within 1000 hours, filing a loss of a mass through everyone 100 hours.

As it is visible from the Table 1, PI, obtained from PAA at the presence of azoles and having higher degrees of cyclization, have the much greater resistance to long-lived action of high temperatures in comparison with usual PI.

The defining value at an estimation of operational properties of polyimide materials has a combination of a high thermostability to other properties of polymer and, first of all, with mechanical and dielectric, sectional about which are reduced in the Table 2.

The mechanical characteristics PI on a basis PAA with benzimidazole are a little bit higher, than at PI on a basis PAA with imidazole, though at last the degree of cyclization is higher, that is bound with partial interchain sewing together, origin of a mesomorphic phase recordings PI in case of benzimidazole. However after thermo-aging of recordings best mecanical properties had of a film PI on a basis PAA with imidazole, and their plasticity at an aging

has not varied, and the toughness even became a little bit higher (for recordings with temperature of ring formation 523 K). Performances noticeably have decreased at an aging at PI on a basis PAA with benzimidazole, however they remained higher, than at PI, obtained without the components.

Table 1 Kinetic parameters of ring-formation of polyamic acids and thermal characteristics of polyimides

Component	Temperature of ring-formation, K		degree of cyclization, %	K, c^{-1}, T(K)		E_a, Kj /mol	Temperature began expansion[1], K(air / argon)	Losses of a mass at isothermal heat (573 K, air), %		
	Begin	end		453	473			100 h	500 h	1000 h
—	403	573	80	4.18×10^{-5}	3.1×10^{-4}	88.03	693 / 793	3.5	13	23.5
Imidazole	383	493	90	1.66×10^{-3}	5.2×10^{-3}	46.34	753 / 818	1.5	7.0	14.8
Benzimidazole	383	523	95	1.87×10^{-4}	9.2×10^{-3}	59.70	743 / —	1.0	5.5	12

Note: 1) On sectional TGA, 5 °/ min

Table 2 Dielectric and deformation-hardness of property of films PI before and after thermo-aging on air (573 K, 100 h)

Component	Up to an aging						After an aging					
	—		Imidazole		Benzimidazole		—		Imidazole		Benzimidazole	
Temperature of ring-formation, K	523	573	523	573	523	573	523	573	523	573	523	573
Degree of cyclization, %	72	80	90	90	85	85	72	80	90	90	85	85
σ_H, MPa	201	220	218	228	235	263	180	173	234	219	196	202
εd, %	18	25	25	37	42	50	19	17	25	25	20,5	20
tgδ	0.019	0.013	0.013	0.009	0.015	0.010	0.011	0.012	0.008	0.010	0.009	—
ρv, 10^{15} om·sm	1.4	5.0	6.0	1.2	3.0	6.0	4.7	5.3	10	8.0	6.0	—
ε	3.49	3.25	3.27	3.05	3.15	3.02	3.23	3.20	2.70	2.63	2.63	—

The dielectric performances in the indicated requirements of an aging appear by more stable. Besides even their some improving after an aging in all cases takes place, that is probable, is bound with ring-formation and removal of tracks of low molecular weight substances.

Thus, the carrying out of ring-formation PAA at the presence of the components of azoles promotes a drop different unit of a structure and, as a corollary it, improving of operational properties PI both in usual, and in extreme requirements at long-lived action of high temperatures in an air medium.

The composites on a basis PI, containing azoles and adhesion components designed, the coats from which have boosted adhesion to various, including semiconducting substratums, high insulant and other properties maintained in requirements of climatic trials. The sectional materials can be utilised in electronic and airspace technique.