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Thermal Stabilization of Polypyromellitimide Films

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SUMMARY: The paper is devoted to the modification of the polyimide based on pyromellitic dianhydride and 4,4'-diaminodiphenyloxide with phosphoric and boric anhydrides. It is demonstrated that, due to the use of phosphorus- and boron-containing polyamidoacid compositions for casting the polyimide films, one can significantly increase their heat resistance without substantial expenditures while, at the same time, preserving the film-forming ability and mechanical properties of the polyimide.

Introduction

The demand for polymers which possess stability to thermal and thermal-oxidative destruction at high temperatures, for use in electric and gas-turbine engines, rockets and high-velocity vehicles for the aerospace industry is well known [1,2]. Polyimides occupy a prominent place among these materials, being a group of polymer materials characterized by high heat resistance, outstanding thermal stability, wide temperature working range good initial deformational, toughness and electrophysical properties. This is due both to the stiffness of polyimide chains and to strong intermolecular interactions. Heat resistance of polyimides can be varied slightly by changing the number of "pin-joints" in the diamine or dianhydride fragments of macromolecules around which the molecular chain can be turned [3]. However, transition from flexible-chain molecules to those with rigid chains, as well as an increase in heat resistance, is accompanied by an inevitable and considerable decrease in elasticity of polyimide materials [4]. That is why thermal stabilization of industrially produced polyimide based on dianhidride of pyromellitic acid and 4,4'-diaminodiphenyl ether is considered to be a separate problem in this field.

In this paper we have tried to improve thermal properties of polyimide films by using phosphorus- and boron-containing polyamidoacid compositions for casting.

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Experimental

Specimens of corresponding polyimide compositions were obtained by introducing an estimated quantity of a corresponding modifying agent (phosphoric or boric anhydride) into polyamidoacid solution in dimethylformamide (DMFA) (specific viscosity of 0.5% PAA solution equaled 1,87) until a uniform composition was obtained. We cast films of the obtained solution on glass pads. After the removal of solvent in vacuum at 293 K the films were taken off the pads and subjected to thermal cyclization by gradual rise in temperature up to 623 K in vacuum.

The study of thermal properties of the obtained film specimens was carried out with a derivatographic device "MOM-OD-103" (Hungary). (100 mg weights, 100 mg weight scale, final temperature 1000 ^{0}C, temperature rise rate amounted to 5 ^{0}C per minute). Toughness, relative elongation at rupture and modulus of elasticity of the polyimide films were determined with a device UMIV-3 (Universal Machine for Fiber Testing) (Russia), (Specimen grip width about 1,5 mm., elongation rate 5 mm per minute, film thickness 50-75 μm).

Results and Discussion

The obtained results are presented below. Table 1 contains thermal characteristics of the obtained films, Figures 1 and 2 illustrate their mechanical properties. The histogram shows relative elongation of the specimens at rupture ε,%. We propose as one of thermal characteristics Q_{600}, relative unit of measurement – heat efficiency of thermal-oxidative destruction of a specimen in the temperature range up to 600 ^{0}C, which is determined according to DTA (Dynamic Thermal Analysis) curves. The temperature range up to 600 ^{0}C has been chosen for the reason that in these conditions heat efficiency is determined by thermal-oxidative destruction of macromolecules, whereas at higher temperatures destruction processes overlap with processes of substantial structuring, which are also exothermic [5].

As Table 1 demonstrates, we are able to substantially improve thermal properties of the films. In the case of P_2O_5 being the modifying agent, extreme dependency of the temperature of the beginning of thermal-oxidative destruction T_d , thermal-oxidative destruction process activation energy E_d and thermal-oxidative destruction heat in the temperature range up to 600^{0}C

Q_{600} on the quantity of the modifying agent is observed. This allows to estimate the optimum modifying agent concentration which amounts to 3%. In this case toughness σ decreases by 20% (Fig. 1), Td increases by 27^{0}C, and Q_{600} is three times smaller. Quite satisfactory results are also obtained by introducing 1% of P_2O_5 into polyamide composition: in this case toughness is reduced by 5% only, and T_d equals 517 ^{0}C.

Table 1. Thermal properties of modified isotropic polyimide films

Modifying agent content	P_2O_5			B_2O_3		
	T_d, ^{0}C	E_d, kJ/mol	Q_{600}, r.u.	T_d, ^{0}C	E_d, kJ/mol	Q_{600}, r.u.
0 %	495	143	1,0	495	143	1,0
1 %	517	151	0,51	508	156	0,79
3 %	522	153	0,33	528	170	0,73
5 %	511	145	0,64	530	180	0,54
7 %	499	142	1,1	532	189	0,43
9 %	496	141	0,85			

An increase in concentration of the introduced B_2O_3 leads to monotonous improvement of thermal properties (Table 1). The introduction of 5% B_2O_3 allows to increase T_d by 35^{0}C, to decrease the quantity of heat given off during thermal-oxidative destruction by 45%, and to increase the value of activation energy of the process Ed by 26%. However, at the same time toughness is decreased by 1/4 and the modulus of elasticity by 42% (Fig. 2). Mechanical properties of films containing 7% of B_2O_3 were not investigated, as the specimens underwent destruction during imidization.

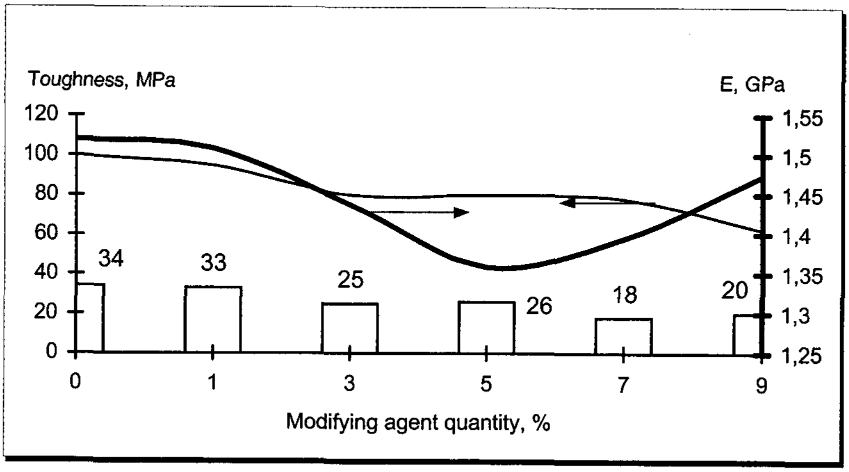

Fig.1. Mechanical Properties of PI films modified with P_2O_5 (The histogram shows relative elongation of the specimens at rupture ε,%)

The mechanism of the stabilizing effect of phosphorus- and boron-containing compounds probably has a many-faceted nature and varies with experimental conditions and a specific character of the stabilizer. The increase in heat resistance must be connected to the formation of a spatial network in the polyimide because of a supposed interaction of oxygen in ≡P=O и —B=O groups of phosphoric and boric anhydrides correspondingly with amide groups of polyamidoacid macromolecules during the process of thermal curing [6].

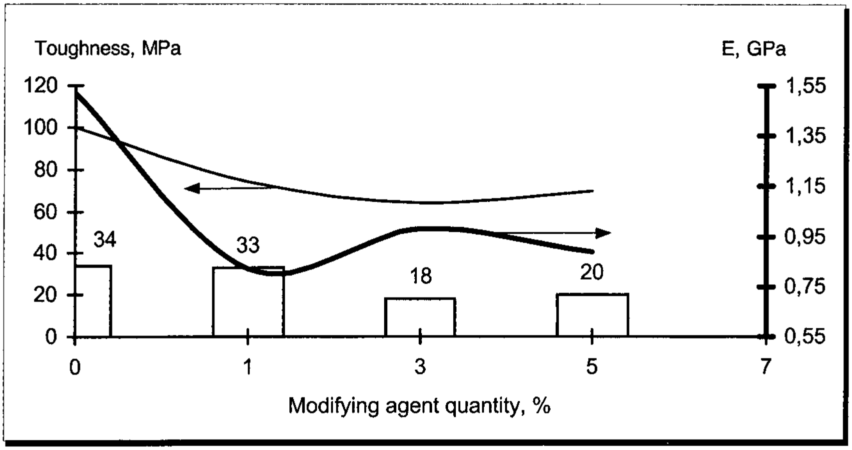

Fig.2 Mechanical Properties of PI films modified with B_2O_3 (The histogram shows relative elongation of the specimens at rupture ε,%)

Besides, there is a reported view that phosphoric and boric anhydrides can form a protective monomolecular layer on the surface of polymer, hindering oxygen access [7].

Conclusions

Thus the obtained results testify to the fact that chemical modification of polyimides with phosphoric and boric anhydrides allows to considerably improve their heat resistance without any substantial material expenditures, at the same time preserving the film-forming capacity and mechanical properties of the polyimide.

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