

MECHANICAL AND THERMAL PROPERTIES OF FULLERENE-CONTAINING POLYIMIDE FILMS

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ABSTRACT

The influence of fullerenes C₆₀ and C₇₀ introduced into a solution of poly-(4,4'-diphenyloxy)pyromellitimide acid on the mechanical and thermal properties of poly-(4,4'-diphenyloxy)pyromellitimide films has been studied.

Keywords: Fullerene C₆₀, Fullerene C₇₀, Poly-(4,4'-diphenyloxy)pyromellitimide acid, Poly-(4,4'-diphenyloxy)pyromellitimide.

Introduction

Polyimides containing fullerenes are promising materials for the creation of new solar cells [1], as well as various optical systems using laser and IR radiation [2].-Fullerenes are known for their use as inhibitors of the reactions of thermal and thermo-oxidative destruction of flexible-chain polymers – polymethyl methacrylate, polystyrene, polyethylene oxide and high-molecular compounds with higher chain rigidity [3, 4]. No information has been found regarding whether the strength and thermal properties of polyimide films change when the polymer is modified with fullerenes.

The purpose of this work is to establish the dependence of the deformation-strength properties and thermal-oxidative stability of poly-(4,4'-diphenyloxy) pyromellitimide (PI) films on the content of C₆₀ and C₇₀ fullerenes.

Experimental technique

Poly-(4,4'-diphenyloxy) pyromellitimide was synthesized by a two-step polycondensation method. In the first stage, a 13% solution of poly-(4,4'-diphenyloxy) pyromellitimide acid (PAA) was prepared by reacting pyromellitic acid dianhydride with 4,4'-diaminodiphenyloxy (Fig. 1) at a temperature of 15 °C in dimethylformamide:

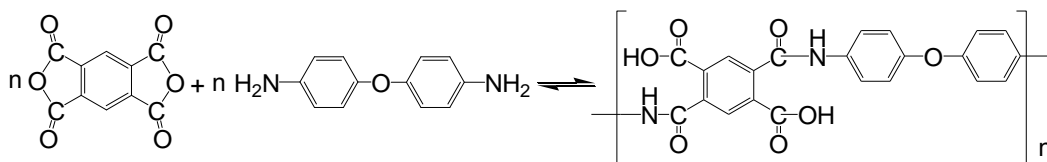


Fig. 1. Scheme for the synthesis of poly-(4,4'-diphenyloxide) pyromellitimic acid.

Subsequently, calculated amount of fullerene solution in xylene was added to the PAA solution. The fullerene content varied at 0.05;0.1;0.2 and 0.5% by weight of PI. Fullerenes C₆₀ and C₇₀ with a main substance content of 99 and 98%, respectively, were used. Films were cast from the solution of fullerene-modified PAA on a glass surface, dried, removed from the substrate, and subjected to cyclization in a vacuum (Fig. 2) with a stepwise temperature increase from 20 to 280°C:

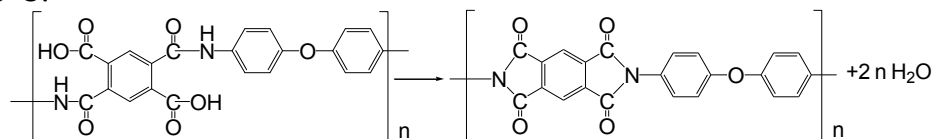


Fig. 2. Scheme of cyclization of poly-(4,4'-diphenyloxide) pyromellitimic acid.

Tests of the deformation-strength properties of isotropic films of fullerene-containing PI and control samples were carried out on a tensile testing machine 8001 (China). The sample had a clamping length of 50 mm, a width of 5 mm, a thickness of 0.02 mm, and a deformation rate of 100 mm/min. The values of tensile strength (σ , GPa), elongation at break (ε , %), and elastic modulus (E , GPa) for PI films represent the arithmetic average of 10 measurements, with a measurement error ranging from 5% to 7%.

Resistance to thermal-oxidative destruction was assessed thermogravimetrically on a NETZSCH STA 449C thermal analyzer (Germany) under dynamic conditions with a sample heating rate of 5 degrees/min in the temperature range from 20 to 1000°C. The temperature of the onset of polymer main chain destruction (T_d) served as a measure of thermal stability, determined by averaging data obtained from the differential thermal analysis and thermogravimetric analysis curves.

Results and its discussion

Figure 3 illustrates the dependencies of the tensile strength of PI films from the fullerene content C₆₀ (curve 1) and C₇₀ (curve 2), which have a limiting character. The maximum strength value is achieved with a fullerene content of 0.1% by weight of PI and practically does not change with increasing amount of modifier. The greatest increase in strength (1.6 times) is observed with the introduction of C₆₀ fullerene in an amount of 0.1 to 0.5%. In contrast, PI films modified with equivalent amounts of C₇₀ fullerene, the strength of the samples compared to the control unmodified sample increases by almost one and a half times.

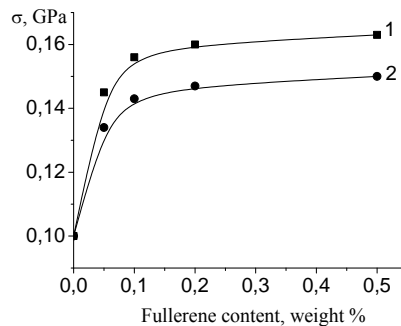


Fig. 3. Dependence of the tensile strength of PI films from the fullerene content C₆₀ (1) and C₇₀ (2)

The elastic modulus, determined by extrapolating the stress at an elongation of 1-2% to an elongation of 100%, increases by almost 80% for films containing 0.1% fullerene C₆₀ and nearly 30% for C₇₀ (Fig. 4). The elastic modulus of the film modified with the maximum amount of C₆₀ fullerene is twice as high as that of the control sample, while for C₇₀ fullerene it increases only by one and a half times.

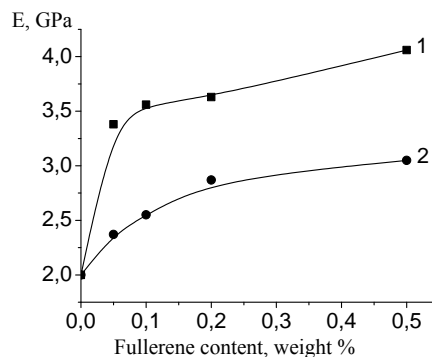


Fig. 4. Dependence of the elastic modulus of PI films from the fullerene content C₆₀ (1) and C₇₀ (2)

The elasticity of the films, assessed by the values of relative elongation at break, decreases by almost half for PI containing 0.5% C₆₀ fullerene, and only by 38% at the same concentration of C₇₀ fullerene (Fig. 5).

Table 1 shows the temperature of the onset of thermal-oxidative destruction of the main chain of the polymer T_d, the temperature of 5-, 10- and 50 % weight loss for samples T₅, T₁₀, T₅₀, the temperature of the maximum rate of destruction T_{max} depending from the concentration of fullerenes C₆₀ and C₇₀ for films modified PI. The temperature at which the destruction of a polymer modified with C₇₀ fullerene begins is 5–10 °C higher than that of a polymer containing C₆₀ fullerene, and approximately 15–25 °C higher than that of an unmodified sample. Temperatures T₅ for samples with C₇₀ fullerene are higher by 5 – 10 °C than with C₆₀, and by 20 – 35 °C, than the same indicator for the control sample.

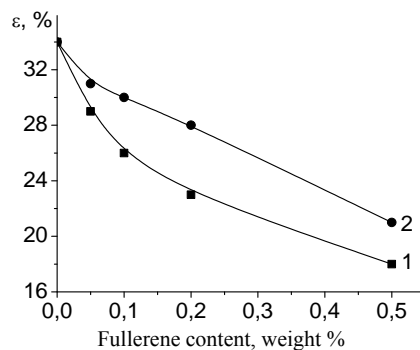


Fig. 5. Dependence of relative elongation at break of PI films from the fullerene content C₆₀ (1) and C₇₀ (2)

Table 1. Thermal-oxidative stability of PI films modified with fullerenes.

Fullerene type	Fullerene content, %	Temperature, °C				
		T _d	T ₅	T ₁₀	T _{max}	T ₅₀
No modifier		520	495	545	585	720
C ₆₀	0,05	530	510	550	585	725
	0,1	530	515	550	585	730
	0,2	535	520	555	585	730
	0,5	535	520	555	590	735
C ₇₀	0,05	535	515	555	590	725
	0,1	535	520	555	590	730
	0,2	540	525	560	590	735
	0,5	545	530	560	595	740

T₁₀ and T₅₀ are characterized by approximately the same patterns; the intervals of temperature increase range from 5 to 20 °C. The temperatures corresponding to the maximum destruction rate of the modified samples are nearly identical to the T_{max} of the unmodified polymer; the largest increase is 10 °C. The analysis of the data in Table 1 suggests that the introduction of fullerenes into the PI matrix increases thermal-oxidative stability, and the C₇₀ fullerene is a stronger inhibitor of destruction reactions.

The increase in the thermal and strength properties of PI films in the presence of small amounts of fullerene can be explained by both the donor-acceptor interaction of the π -electron system of fullerene with aromatic rings, five-membered imide rings and oxygen atoms of the amine component of the macromolecule [4], as well as the formation of covalent chemical bonds between molecules polymer and fullerene. It is known [5] that the chemical properties of fullerenes are fundamentally different from the properties of aromatic compounds.

The presence of isolated multiple bonds in six-membered rings allows us to consider fullerene as an electron-deficient olefin system, characterized by nucleophilic addition reactions. Amines, amides, amino acids, cyanides and other compounds are added to the fullerene with the opening of double bonds. PAA macromolecules contain amide groups in the main chain and primary amino groups at the end. Therefore, at the stage of modification and in the process of cyclization of PAA, nucleophilic addition reactions at the fullerene double bonds of terminal amino groups, as well as amide groups of PAA macromolecules. These reactions can lead to an increase in

molecular weight and the formation of a three-dimensional structure of the polymer, which together leads to a change in the properties of PI films.

Fullerene C₆₀ proved to be a stronger structuring agent compared to fullerene C₇₀, which led to a greater increase in strength and elastic modulus with a simultaneous decrease in elongation at break. At the same time, the thermal characteristics of PI modified with C₆₀ fullerene are lower than those obtained using C₇₀ fullerene. This is due to the fact that during the formation of a network structure, non-cycled defective units appear at the network nodes, reducing the thermal stability of the polymer, and the more efficient the PI structuring process, the more defective groups accumulate in it [6]. In addition, C₇₀ fullerene has demonstrated more effective inhibition of thermal-oxidative destruction reactions compared to C₆₀ fullerene [3].

Thus, the introduction of C₆₀ and C₇₀ fullerenes into the poly-(4,4'-diphenyloxide)pyromellitimide matrix in an amount ranging from 0.05 to 0.5 % leads to an increase in the deformation-strength properties and thermal-oxidative stability of isotropic films.

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FULLEREN TƏRKİBİ OLAN POLİMİD PLYONKALARININ MEXANİKİ VƏ TERMİK XÜSUSİYYƏTLƏRİ

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XÜLASƏ

Poli-(4,4'-difeniloksid)piromellitamid turşusunun məhluluna daxil edilən fulleren C₆₀ və C₇₀-in poli-(4,4'-difeniloksid)piromellitimid plyonkalarının mexaniki və istilik xüsusiyyətlərinə təsiri tədqiq edilmişdir.

Açar sözlər: Fulleren C₆₀, Fulleren C₇₀, Poli-(4,4'-difeniloksid)piromellitamid turşusu, Poli-(4,4'-difeniloksid)piromellitimid

МЕХАНИЧЕСКИЕ И ТЕПЛОВЫЕ СВОЙСТВА ФУЛЛЕРЕНОСОДЕРЖАЩЕЙ ПОЛИМИДНОЙ ПЛЕНКИ

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РЕЗЮМЕ

Изучено влияние фуллеренов C₆₀ и C₇₀, введенных в раствор поли-(4,4'-дифенилоксид)пиromеллитамидной кислоты, на механические и термические свойства пленок поли-(4,4'-дифенилоксид)пиromеллитимида.

Ключевые слова: Фуллерен C₆₀, Фуллерен C₇₀, Поли-(4,4'-дифенилоксид)пиromеллитамид, Поли-(4,4'-дифенилоксид)пиromеллитимид