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COMPOSITE MATERIALS BASED ON ARYLALICYCLIC COPOLYIMIDE WITH ADDITIVES OF POLYETHYLENE GLYCOL

Abstract. Composite films of various compositions from copolyimide based on tricyclodecene tetracarboxylic and diphenyloxytetracarboxylic acid dianhydrides with polyethylene glycol additives were obtained. Using IR spectroscopy, it was found that polyethylene glycol is well combined with copolyimides, forming H complexes on functional groups of PEG and residual amide acids. The thermal and mechanical properties of the obtained composite films are determined. It is shown that PEG additives contribute to an increase in thermal stability, improve strength properties of composite films in comparison with copolymer, while elasticity has acceptable values for such a material.

Keywords: aromatic dianhydride, alicyclic dianhydride, copolyimide, polyethylene glycol, composition, film.

Introduction. At present time, new polyimide materials developed that possess a set of properties that satisfy the majority of requirements for materials used in the electrical engineering industry, including energy-saving technologies [1, 2]. Among of them there are materials based on polyheterocycles of alicyclic structure, including dianhydrides of tricyclodecene tetracarboxylic acids and various diamines, due to their high hydrolytic stability, resistance to aggressive media, high level of electrophysical characteristics [3, 4]. However, these polymers are characterized by lower thermal stability comparatively to aromatic analogs. To production the composite materials with the necessary properties that facilitate their use as a matrix in micro- and nanoelectronics, electrical engineering, integrated optics and other optical technologies, as products with unusual photosensitive, magnetic, heat-conducting properties, modification of (co) polyimides with various plasticizing and inorganic additives are made [5].

In this work, modification of (co) polyimides based on dianhydrides of tricyclodecene tetracarboxylic, diphenyloxydetetracarboxylic acids and diaminodiphenyl ether by polyethylene glycol was carried out. This approach extends practical possibilities of both alicyclic and aromatic homo- and copolyimides [6].

EXPERIMENTAL PART

4,4'-diaminodiphenyl ether (DADPhE) was purified by sublimation in a vacuum at 0.8 atm. and temperature 202 °C, $t_{\text{melt.}} = 186\text{--}188$ °C.

Tricyclo-(4,2,2,025) dec-7-ene-3,4,9,10-tetracarboxylic acid dianhydride (benzene adduct – AB) was purified by boiling in acetone (grade ch.p.), followed by heating for 2 hours in a vacuum at 0, 8 atm. and a temperature of 200 °C, ($t_{\text{melt.}} = 350\text{--}352$ °C).

Dianhydride 3,3', 4,4'-diphenyloxydetetracarboxylic acid (DFO) was purified by heating in a vacuum of 0.8 atm. at 230 °C, $T_{\text{melt.}} = 220\text{--}221$ °C.

Dimethylacetamide (DMAA), methylpyrrolidone (MP), acetone, ethyl alcohol, dimethylformamide (DMFA) was purified according by known procedures [7, 8].

Polyethylene glycol (PEG) from Aldrich (USA), $M = 2000$ (grade ch.p.), was used without additional purification.

Copolyimides based on AB, DFO and DADPhE at the initial ratio AB:DFO = = 90:10 (CPI1) and 85:15 (CPI2) mol. % were prepared by a single-stage copolycondensation in MP in the presence of pyridine (6 wt. %). As catalyst, a gradual increase in the reaction temperature from 90 °C (at this temperature it was held for 0.5 h) to 140 °C (3.5 h, respectively), the monomers concentration in the solution was 40 wt. %.

Compositions based on CPI1, CPI2 with PEG were obtained by adding a solution of PEG in MP (5 wt. %) in the calculation of 0.5–2 % by weight in a solution of CPI1, CPI2 (40 wt. % in MP) at temperature 60 °C with permanent stirring for 1.5 hours.

Films based on CPI and CPI+PEG compositions were formed by watering solutions of copolyimide and compositions based on it on glass surfaces; in order to remove the solvent, the films were pre-dried by heating in a drying oven at the temperature 90 °C during 0.3 hours. After it heat treatment was carried out at the temperature range from 140 to 250 °C in air for 1.5 hours.

IR-Fourier spectra of copolyimide and composite films based on it were recorded on a Nicolet 5700 Spectrometer.

The thermal properties of copolyimide and composite films were investigated by the methods of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a Mettler Toledo TGA/SDTA 851c and FP85 TA Cell device at constant heating rate of 4 and 8 °C/min, from which the temperature of the beginning of decomposition ($T_{\text{b.d.}}$) and glass transition ($T_{\text{g.t.}}$) of the samples was determined.

The mechanical properties of the films - tensile strength ($\sigma_{\text{t.s.}}$) and elongation (l), for samples measuring 10×10 mm², 0.45–0.55 μm thick, were studied on a Com-Tem Testing Equipment (USA) tensile machine.

RESULTS AND ITS DISCUSSION

PEG was used as the modifying additive to the copolyimide matrix. Polyethylene glycols refer to nonionic surfactants in which polyoxyethylene blocks, as well as terminal hydroxyl groups, can form a composite material [9,10] through a polymer-polymer interaction [11]. PEG is amenable to any methods of processing - casting, extrusion, calendaring, pressing. Yarns and films that have good strength and elasticity can be produced from PEG. Thermo oxidative destruction of PEG lies within the limits of 320–370 °C, which is a good prerequisite for combining with heat-resistant (co)polyimides ($T_{\text{b.d.}} \sim 380$ °C).

The preparation of a composite material based on PEG and CPI was carried out by mechanical mixing of the finished copolymer in which the content of the amide acid groups does not exceed 10–15 % [12], because during the reaction mixture of CPI with PEG, polyamide acid which is formed during copolycondensation of AB, DFO, and DADPhE can be cross linked with terminal hydroxyl groups of the modifier [13].

It was found that by mechanical mixing in alicyclic copolyimide it is possible to introduce up to 2 % by weight of PEG ($M = 2000$). Films in this case are visually smooth, transparent with a smooth surface. The introduction of the molecular weight modifier 8000 in the SPI does not lead to the production of transparent films; compatibility of mixture components is absent.

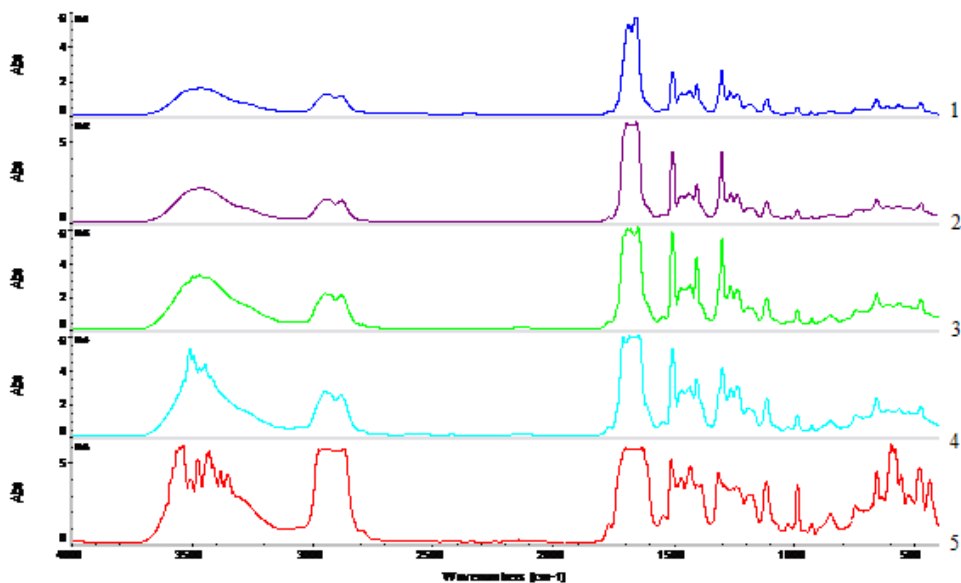
IR spectroscopic study of the obtained compositions and starting polymers was carried out. It was found that when a solution of PEG is introduced into the solution of CPI1 in MP, the characteristic band of the first corresponding to the C–O group is overlapped by the bands of the carbonyl of the imides ring and the amide acid retained in the CPI1 and prescribed by one band in the region of $1681\text{--}1691\text{ cm}^{-1}$.

As the content of PEG in the composite mixture increases, this band expands. In the high-frequency region, the intensity of the broad band ($3200\text{--}3650\text{ cm}^{-1}$) in the spectra of the initial components of the mixture corresponding to the hydroxyl groups of PEG and O–H of the undecycled amido acid groups of the copolymer changes with the addition of PEG. The indicated changes, observed in the spectra during the mixing of polymers, indicate the formation of complexes between the components of the mixture at the level of hydrogen bonds [14]. The formation of H complexes in the mixture is possible between the terminal hydroxyl groups of PEG and the residual acid groups of the amide acid CPI1. Complication in the mixture contributes to the thermodynamic compatibility of the components of the composition.

It was found that containing the PEG in the mixture of polymers about 1–2 wt. % leads to the appearance of copolyimide (1543.5 cm^{-1}) amide groups on the spectra of deformation vibration bands, their intensity increase with increasing PEG in the mixture. This may indicate a decrease in the compatibility of the polymers, i.e. when a PEG of $>1\text{ wt.}\%$ is added to the copolymer, the interaction between the components in the mixture weakens, and bands characteristic of pure polymers are observed in the spectra. In the experiment, however, the revealed decrease in the compatibility of the components does not affect the appearance of the films containing 1.5–2% by weight of PEG, they are obtained in a homogeneous and transparent manner.

The Figure1 shows the IR spectra of SPI2 and compositions based on it, it can be seen that as the PEG content increases, the broadening of the band in the region from $1631\text{ to }1695\text{ cm}^{-1}$, related to the stretching vibrations of the polyethylene glycol C–O and the carbonyl of the imides cycle, is observed in the composition mixture amide acid SPI2. It indicate formation of hydrogen bonds between the residual acid groups of the amide acid in the CPI2 and the terminal

hydroxyl groups of the PEG, as in the case of SPI1. However, in the high-frequency region, for the concentrations of PEG 1 and 2 % by weight, deformation of the absorption bands of stretching vibrations related to the OH groups of the residual amide acid units in the SPI2 and the terminal hydroxyl groups of the PEG in the region 3445–3599 and 3355–3555 cm^{-1} occurs in the composite mixture respectively (figure, curves 4, 5) [14]. This is possible as a result of surface phenomena [10,15,16], manifested in PEG when added to CPI2, since PEG is a non-ionic surfactant. But these phenomena do not reduce the thermodynamic affinity of the two polymers, since films containing 2 % by weight of PEG do not exfoliate [17, 18].



IR spectra:

1 – solution of CPI2 in MP on KBr glass; 2 – compositional mixture based on CPI2 + 0.5% by weight PEG; 3 – CPI2 + 0.75% PEG; 4 – CPI2 + 1% PEG; 5 – CPI2 + 2% PEG

Thus, good compatibility of components achieved. Using IR spectroscopy, found that in the composite mixtures based on CPI1, CPI2 and PEG, the interaction of aryl-acyclic copolyimides with PEG on the functional groups of polymers with the formation of hydrogen bonds occurs, and in the case of SPI2 with the maximum content of PEG exhibits surface activity.

To obtain films of acceptable quality on the basis of the developed compositions, the mode of their heat treatment found experimentally. It was found that the films formed from the solutions of the film compositions must be dried in air at the temperature 90 °C during 30 minutes, then successively raise the temperature to 140 and 250 °C, maintaining in each case during 1 hour, to prevent the film material surface from swelling as a result of rapid heating.

The limitation of 250 °C film annealing is due to the fact that PEG at high temperatures tends to form cross linked structures [15], which reduce the elasticity of the composite film, which is not desirable for the resulting material. As a result of this heat treatment, the surface of the films is smooth, the films retain their integrity and transparency.

The thermal and mechanical properties of the obtained film materials based on CPI1, CPI2 and PEG were determined, and presented in the table.

Thermal and physico-mechanical properties of composite films

Film/ composition	T _{g,t} , °C	T _{b,d} , °C	σ _{t,s} , MPa	l, %
PI	114	380	71	30
CPI1/CPI2+ mass% 0.5 PEG	387/381	402/415	145/179	20/19
CPI1/CPI2+mass% 0.75 PEG	393/375	414/417	160/181	25/18
CPI1/CPI2+ mass% 1.0 PEG	373/370	398/395	129/120	17/17
CPI1/CPI2+ mass% 1.5 PEG	360/352	393/394	125/83	15/13
CPI1/CPI2+ mass% 2.0 PEG	350/355	390/388	82/79	12/11
CPI1/CPI2	388/382	405/408	150/162	20/17

As can be seen from the data presented in the table, increase of both thermal and mechanical properties of the films obtained is observed with an increase of PEG content in the mixture of CPI1 and CPI2 from 0.5 to 0.75 % by weight, further increase the PEG concentration in the mixture provides a certain decrease of these values. Such change in the properties of composite films is due, apparently, to a decrease in the compatibility of the components in the composition.

Thus, new composite films based on CPI1, CPI2 and PEG has been obtained. The optimum content of PEG is 0.75 % by weight, in which the films have improved thermal and strength properties that exceed the similar properties of the original alicyclic polyimide and its copolymer based on AB, DFO and DADPE, and the elasticity is acceptable values for a such material.

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Резюме

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ПОЛИЭТИЛЕНГЛИКОЛЬ ҚОСПАЛАРЫМЕН АРИЛАЛИЦИКЛДІ СОПОЛИИМИД НЕГІЗІНДЕГІ КОМПОЗИТТІ МАТЕРИАЛДАР

Дифенилоксидтетракарбон және үшциклдеценттетракарбон қышқылдарының диангидридтерінің сополиимиді негізінде полиэтиленгликоль қосылумен әр түрлі құрамдағы композициялық қабықшалар алынған. ИҚ-спектроскопия әдісімен сополимердегі қалдық амидоқышқылмен полиэтиленгликольдің функционалдық топтары арқылы Н-комплекс түзе отырып, полиэтиленгликольдің сополиимидпен жақсы әрекеттесетіні анықталды. Алынған композитті қабықшалардың термиялық және механикалық қасиеттері анықталды. ПЭГ қосу композициялық қабықшалардың сополимермен салыстырғанда термиялық және беріктік қасиеттерінің жақсаруына оңықпал ететінін көрсетті, ал серпімділігі осындай материал үшін жарамды болып қала береді.

Түйін сөздер: ароматты диангидрид, алициклді диангидрид, сополиимид, полиэтиленгликоль, композиция, қабықша.

Резюме

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**КОМПОЗИЦИОННЫЕ МАТЕРИАЛЫ
НА ОСНОВЕ АРИЛАЛИЦИКЛИЧЕСКОГО СОПОЛИИМИДА
С ДОБАВКАМИ ПОЛИЭТИЛЕНГЛИКОЛЯ**

Получены композиционные пленки различного состава из сополиимида на основе диангидридов трициклодецететракарбоновой и дифенилоксидтетракарбоновой кислот с добавками полиэтиленгликоля. Методом ИК-спектроскопии было установлено, что полиэтиленгликоль хорошо совмещается с сополиимидами, образуя Н-комплексы по функциональным группам ПЭГ и остаточных амидокислот. Определены термические и механические свойства полученных композиционных пленок. Показано, что добавки ПЭГ способствуют повышению термостойкости, улучшению прочностных свойств композиционных пленок в сравнении с сополимером, при этом эластичность имеет допустимые для подобного материала значения.

Ключевые слова: ароматический диангидрид, алициклический диангидрид, сополиимид, полиэтиленгликоль, композиция, пленка.