

Novel Polymer Composites on the Basis of Arylalicyclic Polyimide Blends. II. Polyimide/Poly(ethylene terephthalate) Blend

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Abstract

The new composite material based on arylalicyclic polyimide and poly(ethylene terephthalate) are being reported. Synthesis and blend preparation methods and their physical-chemical and physical-mechanical properties were investigated. It was observed widening of bands in FTIR spectra, in comparison with the composites reported from our earlier studies. However, it was not detected any physical-chemical interactions between two ingredients of the blend, which could be characterized as a typically compatible polymer blend at the content of PETP up to 25 wt.%. Such new polyimide composite could be utilized as devices, which show both high thermoresistance and stability of polyimide and elastic properties of poly(ethylene terephthalate).

Introduction

Progress in modern technology dictates the necessity of the new composite polymer materials for creation with wide range of specific physical properties. One of the new direction [1] of material investigation is the development of the special polymer mixing technology in order to design the new constructs with high operating performances. Due to the high thermal and radiation stability of polyimides (PIs), there are endless possibilities of obtaining blends based on this class of materials [1-3]. However the formation of composites on the basis of polyimides is not simple task. It is determined by low solubility and double-staged process as well as strong exchange processes of equilibrium system dianhydride + diamine = polyamidoacid [4-5].

The object of this work is to obtain homogenous composite materials based on arylalicyclic polyimide and poly(ethylene terephthalate). This article presents the data on investigation of physical-mechanical and physical-chemical properties of polymer blends and composites. Also it was found out that the spectra of the suggested materials is wider in comparison with the early developed materials. As a result of investiga-

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tion there were obtained composite materials on the basis of arylalicyclic polyimide and poly(ethylene terephthalate) by the way of so-called "mechanical" and "chemical" mixing and worked out the conditions of the films formation. According to the data of IR-spectroscopy it was found out that there are minimal interactions between components mixed, which did not lead to the formation of crystallite units.

Experimental

Synthesis of composite polymer-polymer blends based on arylalicyclic polyimide (PI) and poly(ethylene terephthalate) (PETP or P2) was carried out by the following methods:

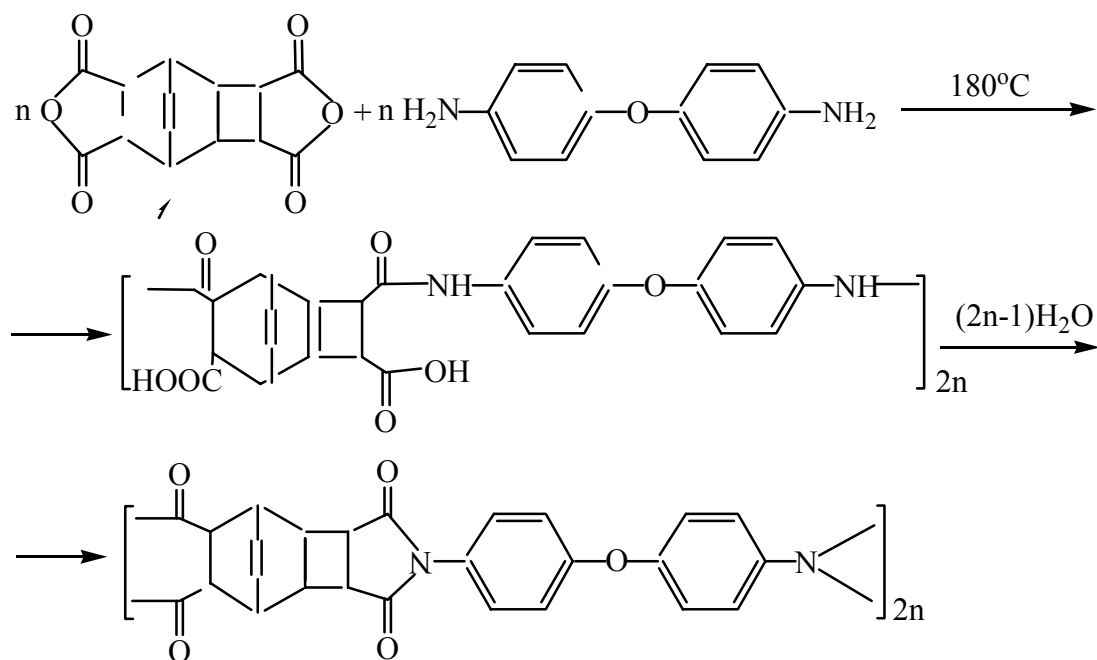
a) mechanical mixing in *m*-cresol in different proportions of polyimide and poly(ethylene terephthalate) (PI:PETP) from 99:1 to 70:30, respectively. High thermal two-staged synthesis of polyimide was prepared based on tricyclodecentetracarboxylic acid. The homogenous blend such obtained was allowed to mix for a period of two hours. This was followed by casting of the films onto the glass plates from the solution. Then the films were dried at 170°C under vacuum.

b) Reaction mixing, the monomers (tricyclodecen-

tetracarboxylic acid and oxydianiline) for the polyimide synthesis were added to the solution P2 and then mixed at the constant rising temperature up to 170°C during five hours. At the end of the reaction, the mixture in *m*-cresol was diluted up to concentration of

6-7% with the same filming procedures.

The main reaction of polyimide is carried out by two-step procedure and based on equilibrium polycondensation of tricyclodecetetra-carboxylic acid with oxydianiline as following:



The initial product of the reaction is polyamate, which undergoes dehydration at 170°C to form an alicyclic polyimide.

IR-spectra of the films were recorded by using a microattenuated total reflectance attachment MATR-81 (Jasco IR-810, Japan) at the room temperature within region of $400 - 4000\text{ cm}^{-1}$. In addition, PI solution in *m*-cresol, where it is mentioned, was coated directly onto a KRS optical crystal, with a thin film of polymer being formed on the KRS plate after rapid evaporation of the solvent under vacuum at 50°C . Afterwards, the KRS-coated films were held in a vacuum oven at the same temperature for a week to remove all traces of the solvent. In the total reflection method, the $10 \times 30\text{-mm}$ polymer sample was held between a KRS-5 prism and a silicon rubber plate.

Further investigations of the new composites on the basis of PI-PETP there were carried out with small angle X-ray diffraction analysis on the diffractometer DRON-3.

Thermal decomposition of PI, PETP and their blends at different ratios were measured with a TGA/SDTA 851^e (Metler Toledo) at heating rate 4°C per min within the temperature range of $50\text{-}800^\circ\text{C}$ under

air and nitrogen.

Results and Discussion

The IR-spectra of PETP shows characteristic absorption bands in the region of 1735 cm^{-1} , 1110 cm^{-1} and 1220 cm^{-1} , 830 cm^{-1} that are related to valency oscillations of the bonds $\nu(\text{C}=\text{O})$ at 1735 cm^{-1} and $\nu(\text{C}-\text{O}-\text{C})$ at 1110 and 1220 cm^{-1} respectively and to deformation bonds oscillations ($\text{C}-\text{H}$) at 830 cm^{-1} . There are also bands at 1110 cm^{-1} due to ester ($\text{C}-\text{O}-\text{C}$), at 2960 cm^{-1} ($\text{C}-\text{H}$) and also at 1500 cm^{-1} that is related to valency oscillations of the $-\text{C}=\text{C}-$ benzene ring [6].

The Figs. 1 and 2 present IR-spectra of blends PI-PETP. The characteristic band 1240 cm^{-1} due to polyimide in PI-PETP spectra remains unchanged, which indicates that the imide structure remains intact. Based on the analysis of IR spectra, it was observed that there was a shift of the carbonyl absorption peak in the region of 1735 cm^{-1} , as compared to the original IR-spectra of PETP (Fig. 1). There is also a shift of the absorption at 1720 cm^{-1} (the carbonyl group of the polyimide) in the blend, with re-

spect to the same band in original polymer, indicating polymer - polymer interactions. The increase of PETP contents up to 20 wt.% demonstrates an appearance of obvious 3440 cm^{-1} carbamide group of PI, especially for samples of chemical mixing. That could be interpreted as non-cyclized imide groups form of amidoacid structures. However, the rate of two polymer miscibility should be approved from viscosious data and thermogravimetry analysis as well as also because the IR data does not show other serious discrepancies between blend samples prepared by chemical and mechanical ways.

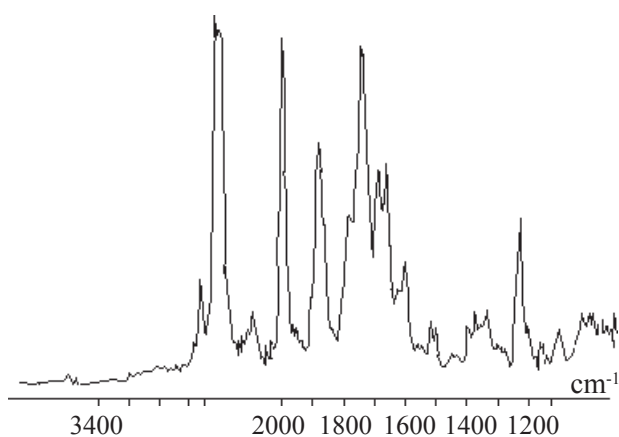


Fig. 1. IR-spectra of PI:PETP at ratio 90:10.

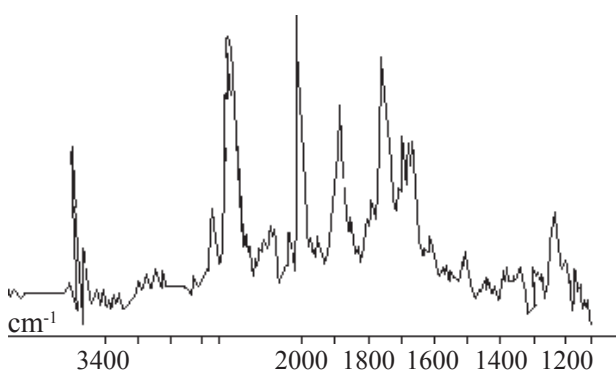


Fig. 2. IR-spectra of PI:PETP at ratio 70:30.

The characteristic solution viscosity of original polymers and their blends is additive, based on the number of components in a blend (Figs. 3 and 4). This indicates that there is no reactive interaction between PI and PETP, which could be led to the formation of a new phase.

X-ray photographs of polymer-polymer blends (PI-PETP) represent the amorphous halo at $\theta = 11^\circ$ that testifies the fact that there has been no formation of any new crystal phase, during the mixing process. Being amorphous the PETP and alicyclic PI do

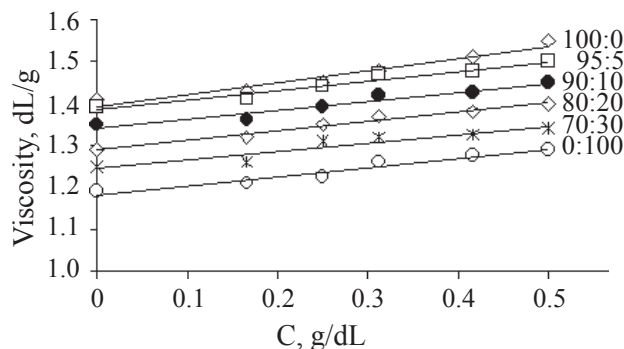


Fig. 3. Viscosity via concentration of PI:PETP blends prepared by mechanical mixing.

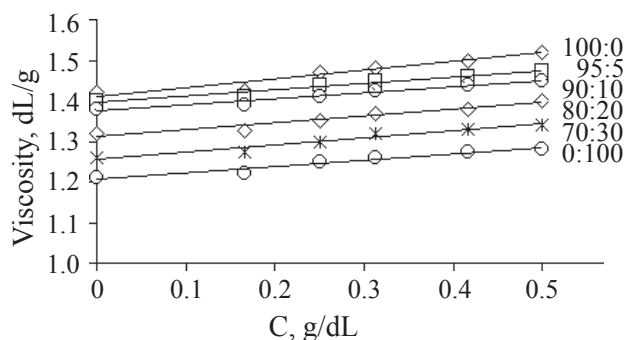


Fig. 4. Viscosity via concentration of PI:PETP blends prepared by chemical mixing.

not form a new phase while mixing as it can be seen from comparing of the X-ray photographs. This fact proves once more that a compatible and definite composite is obtained, while mixing the two components PI and PETP, within the definite limit at PETP content in a blend less 15 wt.%.

The morphology of the film surfaces, which were formed by mechanical and reaction mixing were investigated by optical microscopy that helps to judge the sizes and thin structure of domains. The general picture of blend morphology represents transparent homogenous polyimide matrix with uniformly distributed particles of disperse phase PETP at its content less than 15 wt.% (Fig. 5). The Figure 5 shows that under reaction mixing it is possible to obtain deeper miscibility that results in formation of homogenous and fine-disperse structure. One of the main reasons is condensation of upgrowing polyimide chains along PETP matrix during chemical way of blending. It could cause fine mixing of two polymers at molecular level. Higher content of PETP (above 15 wt.%) promotes the beginning of phase separation which manifests in opaque morphology of blends (data does not show).

Figure 6 presents the derivatives of weight loss thermogrammes of the initial polyimide and its blends

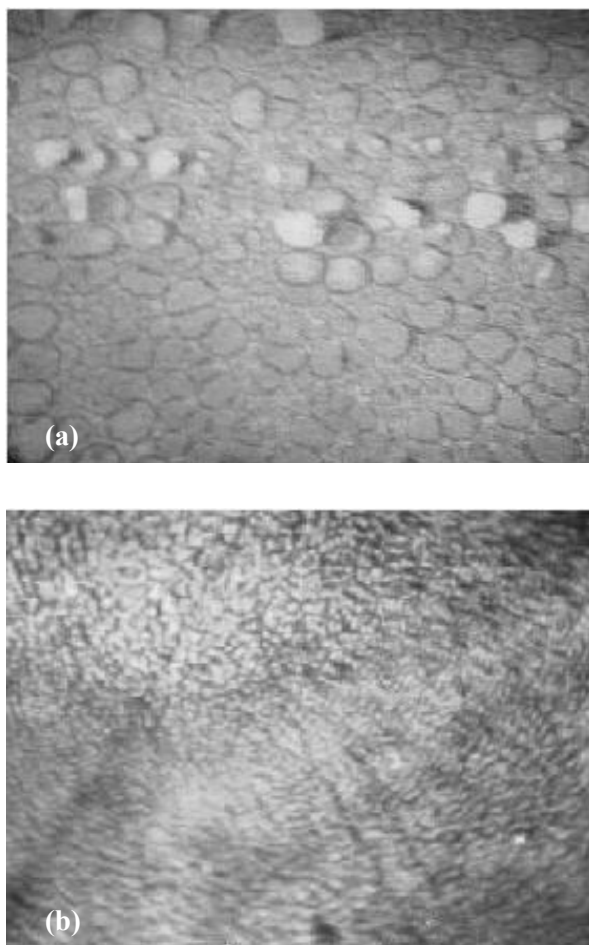


Fig. 5. Microphotos of films on the basis of PI:PETP (ratio 90:10) blends prepared by mechanical (a) and chemical (b) mixing.

at various ratios of PETP 2, 5, 10, 15, and 20 wt.% at the range of temperature within 50-800°C. The addition of PETP up to 10-12 wt.% changes the thermostability of the initial PI hardly. The content of PETP more than 10% leads to obvious destruction of the composites below 400°C, because of tremendous separation of two parts of the composite. Calculated from TGA analysis it was summarized a phase depiction of the prepared PI composites in Table 1.

The addition of P2 into the initial PI causes increasing content of non-cyclized amide groups of PI from 9.4 (PI) to 12.2 wt.% (PI-PETP 1 wt.%). Composites with PETP content between 1-10 wt.% have almost the same fraction of non-cyclized amide group, around 12 wt.%. The increase of PETP content more than 10 wt.% gives rise to low amount of amide group, about 10.2 wt.%, which is close to amide content in the initial PI. It can be speculated that PETP content above 10 wt.% evokes deep separation of two polymers.

Conclusions

Thus, there were obtained the composite materials on the basis of arylalcyclicpolyimide and poly(ethylene terephthalate) and developed the synthesis methods, also there were studied physico-chemical and physico-mechanical characteristics of the composites. It was found that the absorption bands

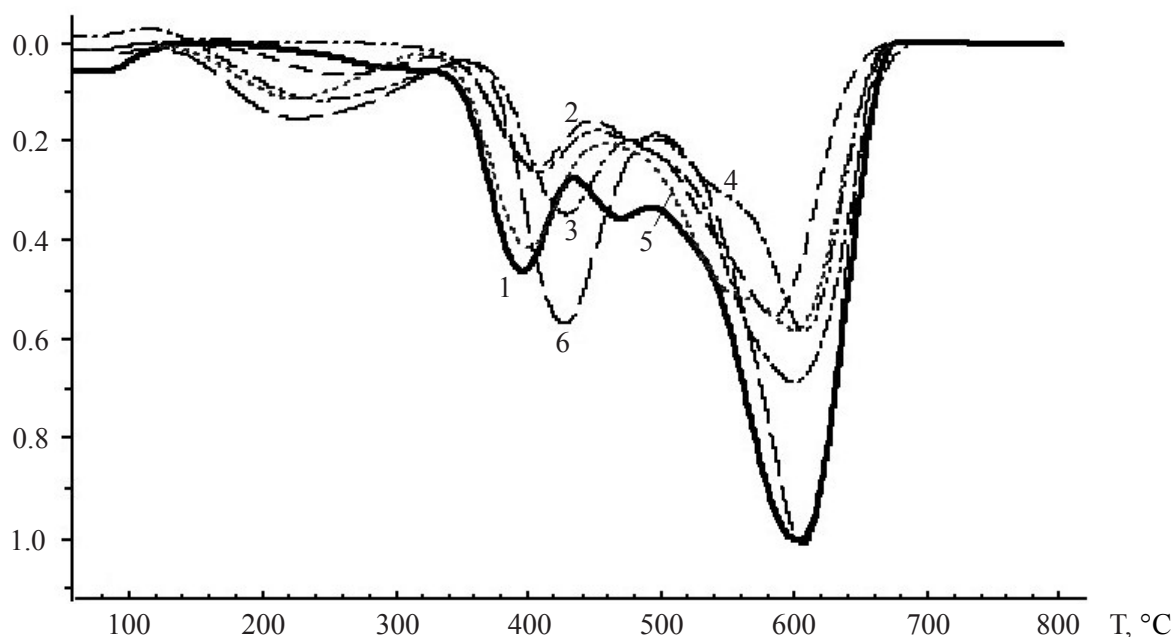


Fig. 6. Derivatives of TGA of PI and its compositions with PETP at different ratios: 1 – PI; 2 – 2 wt.% PETP; 3 – 5 wt.% PETP; 4 – 10 wt.% PETP; 5 – 15 wt.% PETP; 6 – 20 wt.% PETP.

Table 1
TGA data of PI composites of chemical mixing

Composite	Imide group content, wt. %	Amide group content, wt. %	PETP content, wt. %	
			by gravimetry	by TGA
Homopolyimide	90.1	9.6	-	-
PI-PETP 1%	86.1	12.1	1.05	1.15
PI-PETP 2%	83.8	12.0	2.1	2.25
PI-PETP 5%	80.5	11.7	5.1	7.7
PI-PETP 10%	77.9	11.8	10.2	10.3
PI-PETP 15%	74.2	10.4	15.3	14.9
PI-PETP 20%	65.7	10.1	20.4	24.3
PETP	-	-	-	94.9

of carbonyl function of the composites are broader than ones of the materials obtained before. Without forming of crystallite the blend could be characterized as compatible mixture with an appropriate miscibility up to 10 wt.% of PETP. Above this content the phase separation of both PETP and PI. It could be an ideal candidate for the preparation of metallized films with broadened physico-mechanical properties as well as with high reflectivity and electroconductivity. However, mechanical performances of the prepared blends are on the current investigation.

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References

1. S. Kudaikulova, G. Boiko, B. Zhubanov, N. Ashurov, O. Figovsky, M. Abadie. Formulation of polyimide macromolecular blends by one step matrix polycondensation. *Sci. Israel-Technol. Adv.* 1:3 (1999).
2. T. Agag, T. Takeichi. Synthesis and characterization of epoxy film cured with reactive polyimide. *Polymer.* 40:6557 (1999).
3. K. Gaw, M. Kikei, M. Kakimoto, Y. Imai. Preparation of polyimide-epoxy composites. *Reac. & Funct. Polym.* 30:85 (1996).
4. E. M. Woo, S. N. Yau. Peculiar glass transition behavior and miscibility in a binary mixture comprising amorphous poly(ether imide) with semicrystalline poly(butylene terephthalate). *Macromol.* 30(12):3626 (1997).
5. M. Zuo, T. Takeichi. Preparation and characterization of poly(urethane-imide) films prepared from reactive polyimide and polyurethane prepolymer. *Polym.* 40:5153 (1999).
6. Gordon, R. Ford. *Sputnik Chimica*. Mir, Moscow. 1976, p. 529. (in Rus.)

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