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Novel Polymer Composites on the Basis of Arylalicyclic Polyimide Blends. I. Polyimide/Polycarbonate & Polyimide/Polysulphone Blends.

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Abstract

The new composite materials based on dianhydride of tricyclodecentetracarbon acid and oxydianiline with two other thermally stable polymers, such as polycarbonate and polysulphone, are being reported. The synthesis of the polyimide blends was done through two ways: mechanical mixing of two homopolymer ingredients; and the so-called chemical mixing of polyimide comonomers with the above-mentioned polymers. The physico-chemical and physico-mechanical properties have been manifested in a broadening of their performance characteristics. It was not found any physical-chemical interactions between the two ingredients of the blend, which indicates the formation of a typical compatible polymer blend with an appropriate miscibility. Such new polyimide composite could be an ideal candidate for the preparation of reflective and conductive metallized polyimide blend films with wide mechanical performances.

Introduction

In recent years the technologies applied in electric energy, microelectronic and aerospace fields and working out the modern devices require the development of the new polymer materials with high elasticity and strength, thermal stability and refine ability. Such polymers could provide steady work of electric and electronic equipment. One of the contemporary directions of material investigation [1,2] is development of the special technology of material mixing in order to design blends with high operating characteristics. In this regard, creation of the polymer blends on the basis of polyimides (PI) offers several advantages because of their high thermal and radiation stability. This is due to the presence of the phenyl and imide groups in the main chain [2-5].

In this article there are experimental data of the composite polyimide materials based on tricyclodecentetracarbon acid dianhydride and oxydianiline with other thermally stable polymers (P2), such as polycarbonate (PC) and polysulphone (PS). This enables to create new modern materials for electrical engineering with nano-porous structure.

Experimental

Synthesis of composite polymer-polymer blends was carried out by the following two methods:
1) mechanical mixing in *m*-cresol in different proportions of polymers: polyimide-polycarbonate (PI-PC) and polyimide-polysulphone (PI-PS) corresponding to 90:10, 80:20, 70:30. Upon completion of reaction time, P2 was gradually added into reaction flask wherein high thermal one-staged synthesis of polyimide on the basis of tricyclodecentetracarbon acid was carried out. The mixture was stirred during two hours. The homogeneous liquid was used to cast thin films onto glass plates and the films were dried at 170°C;
2) chemical mixing – for the synthesis of polyimide the monomers (tricyclodecentetracarbon acid and oxydianiline) were added to the solution P2 in *m*-cresol. The reaction was allowed to proceed for five hours at constant mixing and gradual rising of temperature to 170°C. The reaction mixture was diluted with *m*-cresol to obtain a final concentration of 6-7%. The main reaction of polyimide is carried out by two-step procedure and based on equilibrium polycondensation of tricyclodecentetracarbon acid with

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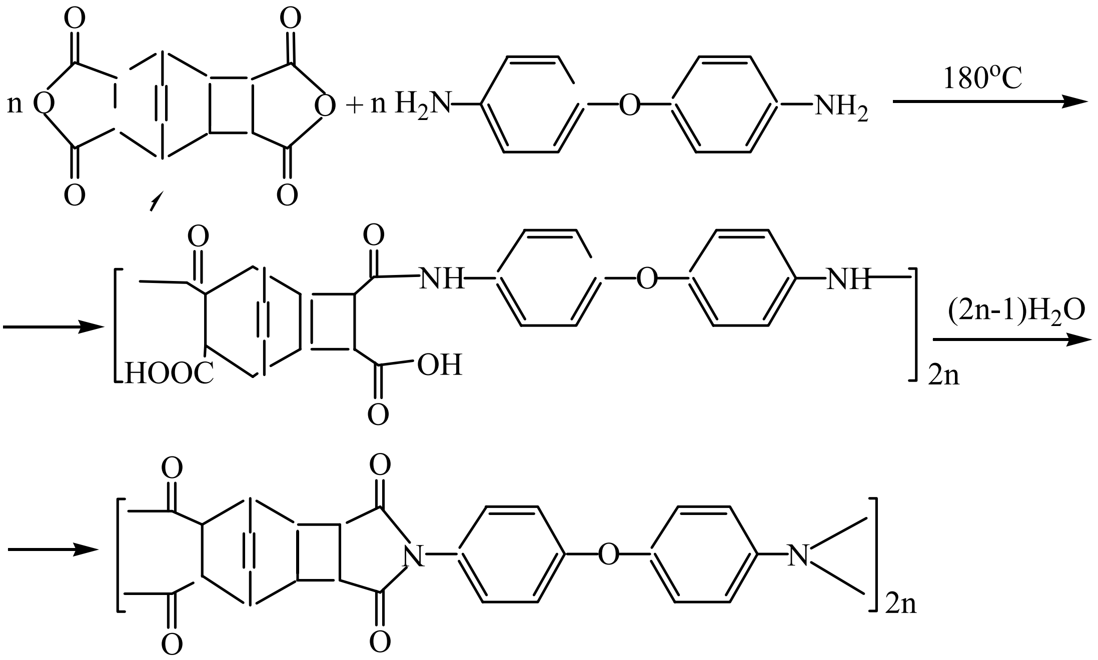
*corresponding author. E-mail: riskakov@mail.ru oxydianiline as following:



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

X-ray small angle diffraction analysis of the new composites on the basis of PI-P2 was carried out on difractometer DRON-3.

Viscosity was implemented by using a Ubellode capillary viscometer from solutions in *m*-cresol at 20°C.

Morphology of the films was investigated by means of optical light microscope Carl Zeiss equipped with Zenith M photocamera.

Results and Discussion

Optimal conditions were chosen for the synthesis of P1-P2 composites. It was shown that P2 could combine with polyimide at low concentrations up to 30%. The amount of P2 more than 30 wt.% leads to strong phase separation, which manifests as non-transparent opaque structure of blend films. Physico-chemical and physico-mechanical characterization of polymer-polymer blends were carried out using viscometry, IR-spectroscopy, optical microscopy and X-ray diffraction analysis, in order to find out the structure and mechanism of interactions between PI and P2 components.

Figs. 1 & 2 present the characteristic viscosities (η_{char}) and their dependence on PI-P2 composition synthesized by mechanical (Fig. 1) and chemical mixing (Fig. 2). It is observed that viscosity depends on the composition and the effect is additive. This indicates no formation of any strong interactions between PI and P2, nor any conformation changes are observed.

X-ray analysis was carried out to obtain information about polymer structure and its conformations, phase changes and conformation of macromolecules that might have occurred as a result of different interactions during mixing. X-ray analysis of PI-P2 blends represents the amorphous halo at θ = 11°, that indicates no formation of the new crystal phase and evidents of polymer mixing at their appropriate miscibility. According to X-ray data the components

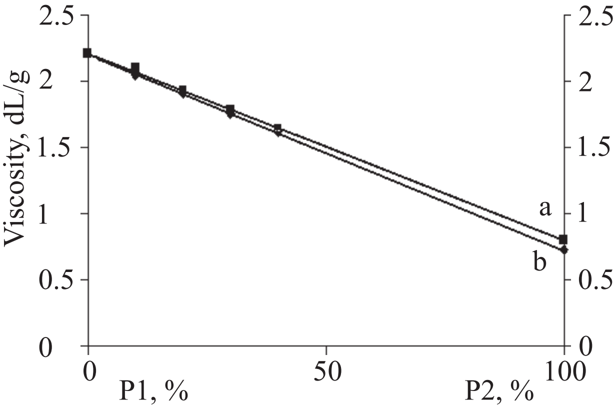


Fig. 1. Viscosity via concentration of PI:PC (a) and PI:PS (b) blends prepared by mechanical mixing.

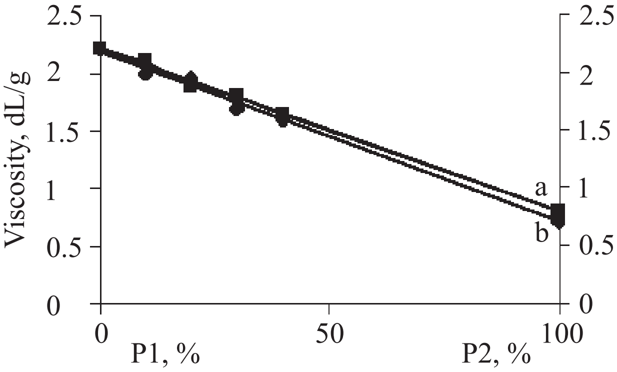


Fig. 2. Viscosity via concentration of PI:PC (a) and PI:PS (b) blends prepared by chemical mixing.

PC, PS and alicyclic PI form unite amorphous phase in their blends.

Microscope data (Figs. 3 and 4) corresponds to mechanical and chemical mixing blends, respectively. The morphology of both modes of blends is homogenous with uniformly distributed particles of disperse phase P2 like domains. The films are trasparent and dark-yellowish. The Figures shows that it is possible to obtain more homogenous and finely dispersed structures with excellent miscibility. Thus making use the chemical mixing microstructure of the films is entirely homogenous and finer than one of mechanical mixing due to better distribution of PI chains among highmolecular weight P2.

There were studied physico-chemical characteristics of the composites on Table 1 for their breaking stress σ and tensile elongation L. [η] represents viscosity of 5 wt.% polymer mixture solution. It was found out that for the blend with P2 contents up to 30 wt.% the homogenous composites with both appropriate miscibility and wide mechanical performances could be formed. Blending of polyimide films leads to formation of more elastic films with reduced strengh and enhanced elongation. Addition of another polymer with good mechanical performances gives rise to a new polyimide blend, which has better me-

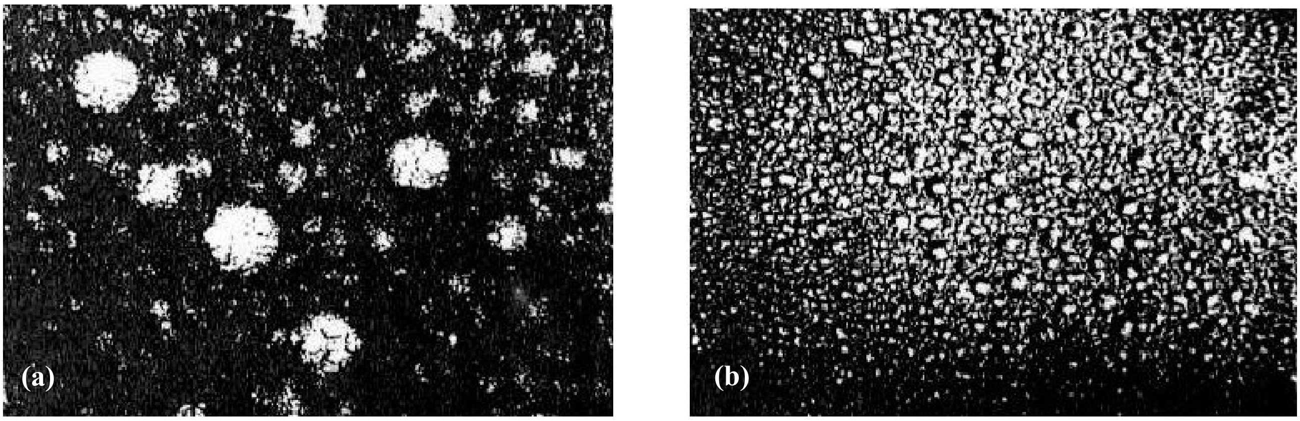


Fig. 3. Microphotos of films on the basis of PI:PC (ratio 90:10) blends prepared by mechanical (a) and chemical (b) mixing. Bar is 100 μm.

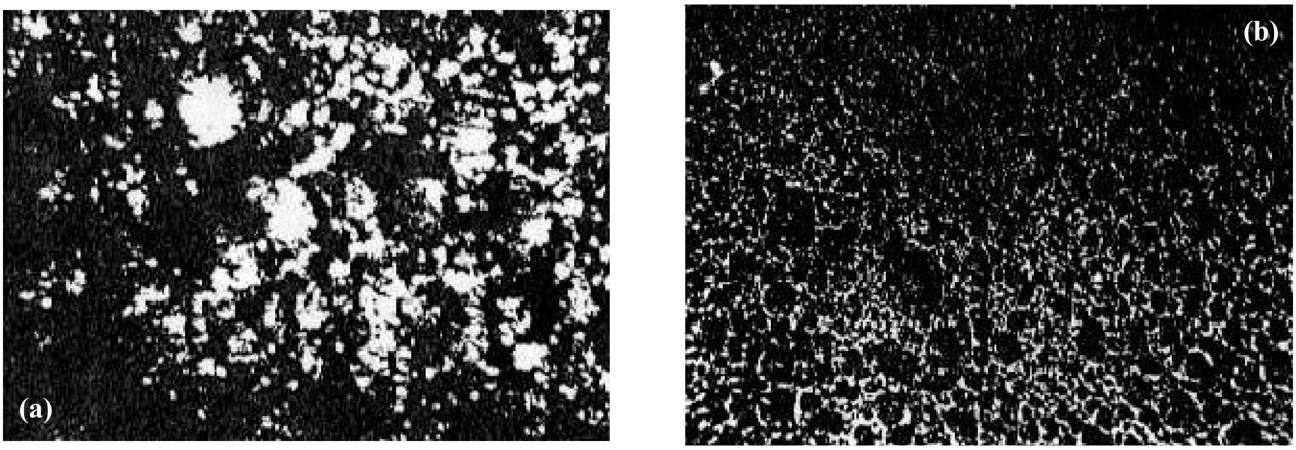


Fig. 4. Microphotos of films on the basis of PI:PS (ratio 90:10) blends prepared by mechanical (a) and chemical (b) mixing. Bar is 100 μm.

chanical stability, while retaining the excellent thermally resistant properties of the polyimide itself.

Table 1
Physico-mechanical performances of homopolymers and their blends

Composition, mol%	[η], dL/g	σ, kg/cm^2	L, %
PI	1.28	1026.6	28.6
PS	0.625	715	75.0
PC	0.68	780	72.0
10%PS : 90%PI	1.21	945.3	29.9
20%PS : 80%PI	1.149	926.3	33.4
30%PS : 70%PI	1.1	897	49.0
40%PS : 60%PI	1.025	802.4	46.3
50%PS : 50%PI	-	798.8	43.8
10%PC : 90%PI	1.225	957.4	36.6
20%PC : 80%PI	1.175	953	44.5
30%PC : 70%PI	1.12	904.5	51.1
40%PC : 60%PI	1.065	875.2	48.2
50%PC : 50%PI	-	827	46.6

Conclusion

By the introduction of certain amount of P2 we could drastically change the final mechanical properties of the resulting PI blend films. With addition of P2 there is strong tendency leading to formation of more elastic films with reduced strength and enhanced elongation.

The developed methods of polyimide mixing allowed avoiding a low solubility of PI in blends as well as carried out the synthesis by means of one step polycondensation.

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