

Prospects for the synthesis and application of copolyimides based on tetracarboxylic acid dianhydride mixtures

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Abstract. The process of obtaining copolyimides by polycondensation based on 3,6-diaminoacridine, 9,9-bis-(p-aminophenyl)fluorene, dianhydride of 2,2-bis-(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane and dianhydride of 3,3',4,4'-tetracarboxydiphenyl oxide are described. The main physico-chemical properties of the obtained products are discussed and the prospects for the use of these soluble and fusible products as a polymer base for the preparation of composite materials are shown.

1 Introduction

Thermoplastics are one of the most promising classes of polymers used to create composite materials, since processing technologies by extrusion or injection molding allow creating parts of complex shape from formulations with dispersed filler under conditions of minimal processing when implementing structural tasks [1-2].

Polyimides as heterocyclic thermoplastic polymers refer to ultra-heat resistant polymers. Due to their performance characteristics thermoplastic polyimides are the most promising thermoplastics for various kinds of composites. Compared to existing large-tonnage industrial polymers such as polystyrene, they have improved thermal resistance, improved mechanical properties retained even at high temperatures, as well as high resistance to aggressive media, including acids, alkalis and radiation exposure [3-5].

Table 1 shows some temperature-dependent properties of polyimides in comparison with known natural and synthetic polymers. Polyimides can be regarded as fairly temperature-resistant polymers, which have a thermosetting polymer matrix with very low creep and high tensile strength and these basic properties are retained for long-term use at temperatures up to 230...250°C and for short-term temperature exposures can be retained even at 500...700°C.

Polyimides include polymeric compounds with imide cycles. Molecular chains of polyimides, in addition to imide links, also contain aromatic nuclei linked by a heteroatom or carbon atom, which, in some cases, gives them unique physical and chemical properties. The synthesis and investigation of new polyimides is of increasing interest, in particular, the synthesis of copolyimides attracts particular attention. The irregular structure of the

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polymer chain giving the polymer an amorphous structure, the presence of polar branches and the presence of mobile hinge groups in the monomer structure, such as a simple ester bond or a keto group, increase the solubility of the polyimide and reduce the processing temperatures, which, compared to rigid chain polyimides, can significantly decrease the material cost of production on the base.

An important problem of using polyimides in obtaining highly dispersed composite materials is their recyclability in products from solution or melt, since these compounds belong to polymers with high chain rigidity and strong intermolecular interactions of polar groups [9-12].

It is known that in order to carry out efficient processing of polymer systems, the molecular weight of the constituent polymer should not be too high and in order to preserve the basic properties of the polymer, there should not be a serious decrease in the molecular weight during processing. Therefore, an urgent task in the field of modern composites is to create easily recyclable polyimides. Such polyimides should have good solubility in organic solvents, a relatively low melting point and thermal stability under prolonged heating [13, 14].

At present several brands of industrial polyimides are known, such as Ultem, Kapton, P84 and some others. These industrial polyimides are used to make high-strength and heat-resistant films, fibers, electrical insulation, structural parts and filtration membranes [15-19].

Table 1. Melting and ignition temperatures of basic natural and synthetic polymers

Polymer material	Melting temperature, °C	Ignition temperature, °C
ABS plastics	88...125	416
Acrylates	91...125	560
Cellulose	49...121	475...540
Nylons	160...275	424...532
Polycarbonate	140...150	580
Polyethers	220...268	432...488
Low pressure polyethylene	107...124	349
High pressure polyethylene	122...137	350
Polypropylene	158...168	570
Polypropylene	100...120	488...496
Polypropylene	85...121	416
Polystyrene	327	530
Polyurethanes	170... 410	450...560
Polytetrafluoroethylene (Fluoroplastic F4)	75...110	435...557
Polyimides	–	228...230
Polyvinyl chloride	–	250
Polyvinyl chloride	–	260...316
Wool		
Cotton		
Rubber		

Properties of commercially available polyimides are insufficient for obtaining a number of special polymeric materials. Therefore, there is an increased interest in copolyimides with irregular, statistical distribution of units of various chemical nature, since irregularity of polymer chain structure gives the copolymer an amorphous structure, and the presence of polar branches and mobile hinge groups in the structure of initial monomers, such as ester

bond or ketone groups, increases solubility of polymer product and also reduces processing temperatures, which in comparison with classical rigid-chain polyimides may significantly reduce the processing temperature.

It should be noted that the presence of molecular so-called "hinge" groups only in the dianhydride fragment in the sopolimide structure can only slightly increase the elasticity of the polymer, slightly affecting the rigidity and brittleness. The introduction of "hinges" only in the diamine fragments allows obtaining strong and elastic films which lack a certain softening point interval. Therefore, it is advisable to use different monomers containing "hinge" groups both in dianhydride and diamine in order to obtain easily processed polyimides, which will significantly increase the flexibility of the molecular chain, which affects the solubility and strength of the polymer. And by using different dianhydrides and diamines and thus obtaining copolyimides, it is possible to influence to a greater extent the solubility, strength, and other physicochemical properties of polyimides, as well as to obtain materials with lower density.

Recent studies show that sopolymides with a large number of hinge groups or with "suspensions" on aromatic nuclei, which can be modified to enhance solubility in the presence of reactive groups, are promising. The synthesis of such polyimides is of particular interest.

The aim of the work was to develop a methodology for the preparation of thermostable organo-soluble or thermally fusible sopolymides for subsequent use as reinforcing binders in the technology of carbon fiber-reinforced plastic composites.

2 Materials and methods

2.1 Raw materials

The reagents used in this work were: 3,6-diaminoacridine (acridine), 9,9-bis-(p-aminophenyl)fluorene (FDPA), 2,2-bis-(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (6FDA) dianhydride, 3,3',4,4'-tetracarboxydiphenyloxide (BTDA) diacid, m-cresol, isoquinoline, N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, chloroform, cyclohexanone, tetrahydrofuran, dichloroethane, 1,1,2,2-tetrachloroethane, toluene, nitromethane and acetonitrile qualification analytically pure for analysis manufactured by Merck and Serva (Germany).

2.2 Methods

The synthesis of polyamido acids was performed in an inert atmosphere at reduced temperature, in various organic solvents, since polyamido acids are unstable at normal and higher temperatures, and the process was further cyclized at elevated temperature for several hours.

The copolyimides were synthesized by polycondensation of two diamines acridine and FDPA with 6FDA or BTDA dianhydride, respectively, as shown in the scheme (Fig. 1).

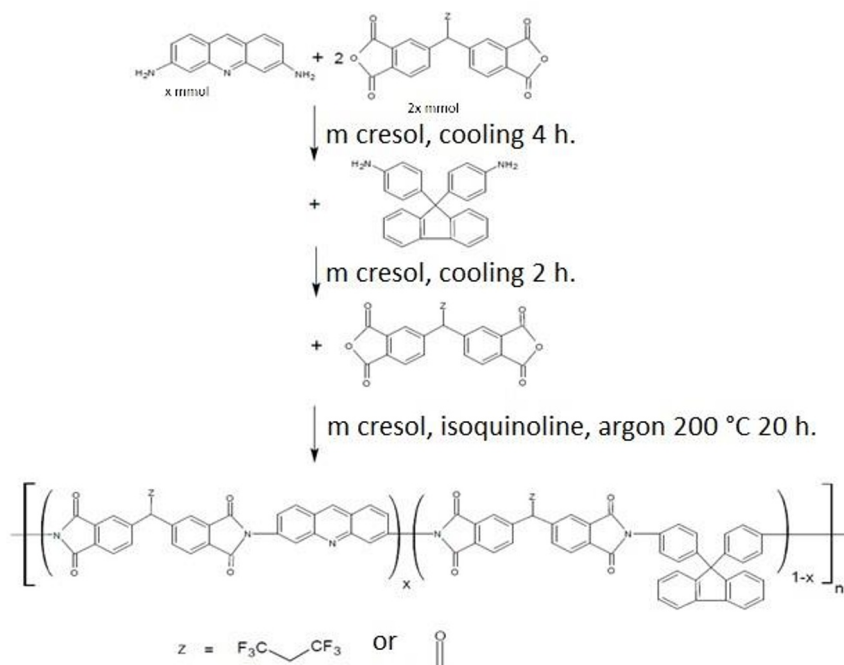


Fig. 1. General scheme of the sopolimide production process

The molar amount of dianhydride 6FDA (or BTDA) was kept constant and the amounts of the two diamines acridine and FDPA were varied while keeping the total molar number of the two diamines equal to the amount of dianhydride. The copolyimides derived from different co-monomers were named AFF x (acridine-FDPA-6FDA copolyimides) and AFB x (acridine-FBPA-BTDA copolyimides), where x ($x = 0, 1, 3, 5, 10, 15,$ and 20) is the mole percentage of acridine content of the sum of the amounts of two diamines.

For example, AFF5 SPI-5 was synthesized in a 50 ml three-neck flask equipped with a magnetic stirrer, a thermometer, and an argon tube. Acridine in an amount of 10.5 mg (0.05 mmol) and 2 ml of m-cresol were added. After complete dissolution of the diamines 44.4 mg (0.10 mmol) of 6FDA was added. The reaction mixture was stirred for 4 h at room temperature. Then 330.8 mg (0.95 mmol) of FDPA was added and the reaction mixture was stirred for another 2 h. Finally, 6FDA in an amount of 399.8 mg (0.90 mmol) was loaded, 4 mL of m-cresol and 0.2 mL of isoquinoline were added. The reaction mixture was stirred, heated to 200°C and purged with a weak current of argon for about 20 h, then gradually (within 1 h) cooled to room temperature. During cooling, the mixture was diluted with m-cresol to keep the reaction mixture in an acceptable fluid state. The polymer product was isolated by precipitation by adding 300 mL of methanol. The precipitate was filtered off and extracted with methanol in a Soxhlet extraction apparatus for 24 h. After drying in vacuo at 80°C for 4 h and at 260°C for 6 h, SPI-5 was obtained as a gray powder in 93.5% yield.

Other copolyimides AFF x and AFB x with indices $x = 0, 1, 3, 5, 10, 15$ and 20 (listed in Table 2) were obtained by the method described for obtaining SPI-5 by changing molar ratios of acridine with FDPA from 1/99 to 20/80. The product yield from the polycondensation reaction was 90...95%. With the increase of acridine content in polyimides the color of the products changed from white-gray to brown.

Solubility of obtained copolyimides was studied in N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, chloroform,

cyclohexanone, tetrahydrofuran, dichloroethane, 1,1,2,2-tetrachloroethane, toluene, nitromethane and acetonitrile.

Co-polyimide films were obtained by irrigation from the solutions followed by drying to a constant weight, up to 0.5 mm thick after drying.

The strength characteristics of the obtained film samples with dimensions of 15 x 250 mm and an average thickness of 0.2 mm were studied using an Instron 3369 (USA) tensile machine according to the standard procedure [22].

The molecular weight of SPI was estimated viscometrically from a 1% solution in dimethylformamide using the Mark-Kuhn-Hauvinck equation $[\eta] = 1.5 \times 10^{-3} M^{0.5}$ [23].

The thermal properties of copolyimides were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal stability of the copolyimides was evaluated by TGA curve measurements in a nitrogen atmosphere at a heating rate of 10°C/min.

3 Results and discussion

Sopolyimides are rather rigid carbon-chain polymers for processing them into a number of useful materials, for example, when obtaining chemically resistant polymer membranes with gas or molecular selectivity, there is a need to use the solubility effect. It was assumed that in the synthesis of copolyimides using a mixture of the initial dianhydrides used, due to the irregularity in the structure of the polymer chain formed, the product would be better soluble in a greater number of organic solvents than in the case of synthesis of copolyimides using only one dianhydride.

Table 2. Solubility of copolyimides based on carboxylic acids dianhydrides in organic solvents

Solvent	Solubility										
	F F0	AF F1	AF F5	AFF 10	AF F20	AF B0	AF B1	AF B5	AFB 10	AFB 15	AFB 20
Tetrahydrofuran	+	+	+	+	+	±	±	±	±	±	±
Cyclohexanone	+	+	+	+	+	+	+	±	±	±	±
Chloroform	+	+	+	+	+	+	+	+	+	+	+
Dichloroethane	+	+	+	+	+	+	+	+	+	+	+
Tetrachloroethane	+	+	+	+	+	+	+	+	+	+	+
Dimethylformamide	-	-	-	-	-	-	-	-	-	-	-
Dimethylacetamide	-	-	-	-	-	-	-	-	-	-	-
Dimethylsulfoxide											
Toluene											
Nitromethane											
Acetonitrile											

+ dissolves; - does not dissolve; ± dissolves partially

To synthesize the target products containing a mixture of tetracarboxylic acids dianhydrides, we used the method for obtaining the product using one of the two dianhydrides, however, with adjustments for the mixture of dianhydrides taken in different ratios. The solubility test results of the obtained copolyimides are shown in Table 2.

Due to the presence of polar fluorinated groups the obtained product became completely soluble in those solvents in which before only partial solubility was shown regardless of the ratio of diamine fragments. Due to this effect, it is possible to form and study films from the obtained copolyimides.

Polyimides are positioned among polymeric materials as sufficiently thermostable compounds, significantly surpassing natural biopolymers in such characteristics. Figure 2 shows the results of thermomechanical tests. It can be concluded from the character of images of all the main curves for the obtained soproliimides that the operating temperature interval without violation of the form and apparently internal structure of polymers is unchanged up to temperatures of 300...320°C that can be used to create appropriate composites operating under high thermal loads.

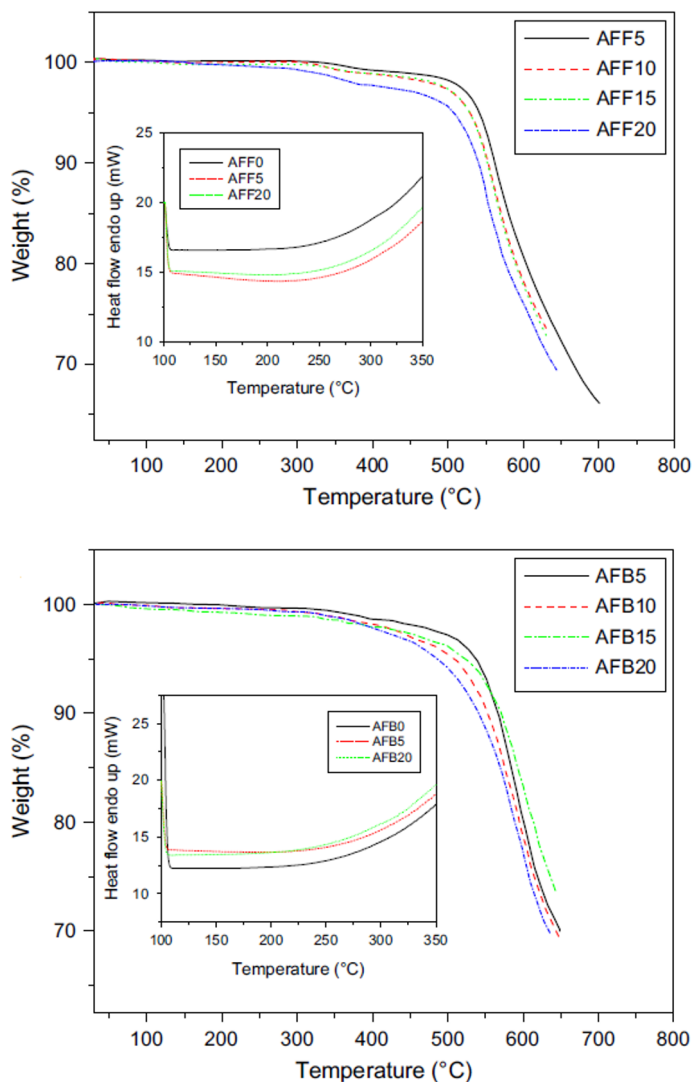


Fig. 2. TGA and DSC (inset) curves of comparolimides in a nitrogen atmosphere at heating rate 10°C/min for TGA and 20°C/min for DSC

The results of viscometric tests to estimate the value of the molecular weight of the polymers obtained showed that the products obtained had a molecular weight in the range from 26 to 175 kDa depending on the time of exposure of the reaction mixture at 200 °C in a current of inert gas. The minimum value of the indicated molecular weight was characteristic for the corresponding holding time of less than 2...4 h, while the heating of the reaction mixture and carrying out the copolycondensation process for up to 20 h resulted in the products with the maximum value of the molecular weight of sopolimide.

Tensile breaking stress σ_p of the polymer films obtained depending on film thickness was in the range from $\sigma_p = 140$ MPa for 0.2 mm thick film to $\sigma_p = 210$ MPa for 0.5 mm thick film, and elongation at break ranged from 5...36%. The values of these physical and mechanical parameters were largely influenced by the solvent from which the films were prepared, thereby potentially varying the microporosity of the polymer system.

4 Conclusions

Hence, the methodology used to obtain functional copolyimides with differently linked fragments from tetracarboxylic acids dianhydrides allows us to obtain synthetic polymeric materials with positive solubility characteristics, providing their further use in creating heat-resistant composite materials.

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