Journal of Thermal Analysis, Vol. 36 (1990) 2329-2338

PREPARATION AND INVESTIGATION OF POLYMER-POLYMER COMPOSITIONS BASED ON POLYACRYLONITRILE AND AROMATIC POLYAMIC ACID

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(Received December 13, 1989)

A modification of polyacrylonitrile (PAN) was carried out. As a result, a polymer compatible (in contrast to common PAN) with polyamic acid (PAA) was obtained. PAA, PAN and their mixtures in solution and in film were investigated by viscometry, mass-spectrometric thermal analysis (MTA), TG and electron microscopy. The physico-mechanical characteristics of the corresponding composite films were obtained.

The search for the paths of further imoprovement in physico-mechanical properties of polyimides (PI) and the desire of a better understanding of the mechanism of the processes controlling intermolecular interaction in the chains of this polymer explain the increasing interest in the study of the compositions of this polymer class both with low molecular weight organic compounds, i.e. with furyl alcohol (FA) [1] and with polymers, such as polyvinylpyrrolidone (PVP) and polyacrylonitrile (PAN) [2, 3]. In this case, properties that are not characteristic of the initial components may appear. Thus, PAA PM in the composition with FA initiates its polymerization. The product of interaction between PAA and PVP subjected to imidization reveals a much higher adhesion to glass and metal and a much higher stability to water, alkalis and acids than the initial imidized PAA.

According to the concepts of the authors of ref. [3], the nature of interaction between PAA and PAN in their mixtures is determined by the presence of nitrile groups in the latter, and the degree of modification depends on the PAA fraction in the composition.

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Since a copolymer of acrylonitrile (AN) and methyl acrylate (MA) has been used in ref. [3], it was of interest to study the interactions by using an AN homopolymer synthesized by using anionic systems because they are known [4] to ensure the possibility of preparing a polymer with a rigorously predetermined MW and narrow MWD.

Experimental

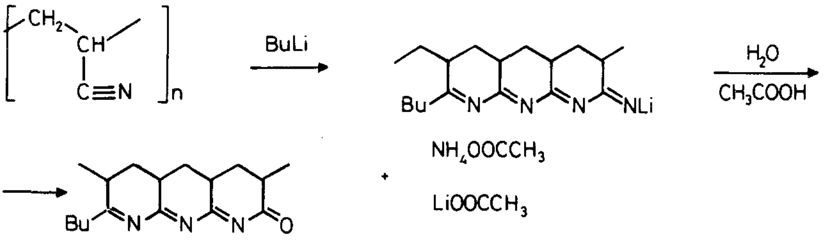
PAA PM was synthesized by a standard procedure [5] by adding pyromellitic dianhydride to a solution of 4,4-diaminodiphenyl ether in dimethylacetamide (DMAA).

A polymer obtained in an anionic system at -50° [6] and $[\eta] = 1.0\text{-}1.5$ dl/g was used as PAN-1.

PAN-1 was modified by n-butyllithium in an inert gas in a dimethyl formamide (DMF) solution at +20° (PAN - 2, $[\eta] = 0.05\text{-}0.15$ dl/g).

The reaction was stopped by adding a solution of acetic acid in DMF. The polymer was precipitated with water, washed in a large amount of water and dried in a thermostat at +70° to constant weight.

With the aid of IR spectroscopy and elemental analysis, carbonyl groups and cyclic structures with imino groups formed according to the scheme were identified:



The solutions for film preparation were obtained by mixing directly a solution of PAA PM in DMAA and a solution of PAN-1 or PAN-2 (total concentration of the dry substance was 10-15%) or by synthesizing PAA PM in a solution of PAN in DMAA. The films (30-40 μm) were formed by the casting procedure and air-dried at 50°.

The films were imidized in air by heating them to 400° at a heating rate of 4 deg/min.

Viscometric investigations were carried out in dilute solutions (0.1-0.5%) with the aid of an Ubbelohde capillary viscometer by a standard procedure. The time of solvent flow was 100.3s.

MTA was carried out with an MKh 1320 instrument (USSR) by a method described in ref [7]. As quantitative and qualitative criteria for the evaluation of PAA cyclodehydration, the data on water elimination were used (temperatures of the start, the maximum and the end of the H_2O peak and its halfwidth).

The film density was investigated by the flotation method in a toluene-carbon tetrachloride (1:1) mixture at 20°. The gas permeability of films was measured with a PGD-01 instrument (USSR).

The thermo-oxidative stability of the samples was determined with a derivatograph in an air flow (50 cm^3/min), the heating rate was 5.0 deg/min, the sample weight was 50 mg and the inert reference substance was Al_2O_3.

Experiments on the determination of density and elastic moduli were carried out with a UMIV-3 (USSR) universal instrument for mechanical and thermomechanical tests. The construction of the instrument ensured the rate of experiments under stretching conditions of 5 mm/min. The error in the measurements of these values was 3%.

The morphology of composite PAA-PAN films was investigated with the aid of electron microscopy. The recording was carried out with a BS-500 "Tesla" instrument (Czechoslovakia). Single-stage coal-platinum replica were studied. They were taken from free surfaces of films etched in a plasma of high-frequency oxygen discharge according to the procedure used in ref. [8]. The shading of Pt was carried out by an angle of 45° to the sample surface.

Results and discussion

Before considering the character of interaction between PAA PM and PAN, it is necessary to deal with the ability of both polymers to give solid complexes with amide solvents.

A system of hydrogen bonds formed in the solvocomplexes of PAA PM has been previously investigated taking as an example pyromellitdianylie acid (PMA) for which crystalline complexes with DMF and N-MP (N-methyl pyrrolidone) have been isolated [9]. X-ray analysis has shown [10] that the DMF molecule is attached to a vacant proton-donor centre, the amide group and is forming a hydrogen bond: O carbonyl DMF...H...amide. More reactive molecules of N-MP displacing DMF from the solvocomplexes actively participate in the formation of intermolecular bonds thus preventing the formation of hydrogen bonds between PMA molecules.

It may be assumed that a similar picture is observed to a considerable extent in the PAA solvocomplexes. It has been shown [11] that a great number of carbonyl-containing compounds compete with the solvent during complexation. Since PAA solvocomplexes contain one solvent molecule per one carboxiamide group [9], with the aid of MTA it is possible to obtain qualitative and quantitative characteristics of the competition of these complexes in the formation of hydrogen bonds. Calculations have been carried out for a PAA PM-PVP system [1]. They made it possible to evaluate quantitavely the number of contacts between PVP and PAA PM molecules (approximately each fifth carboxyamide group interacts with PVP). The structure formed here leads to a considerable change in the properties of polyimide (PI) films.

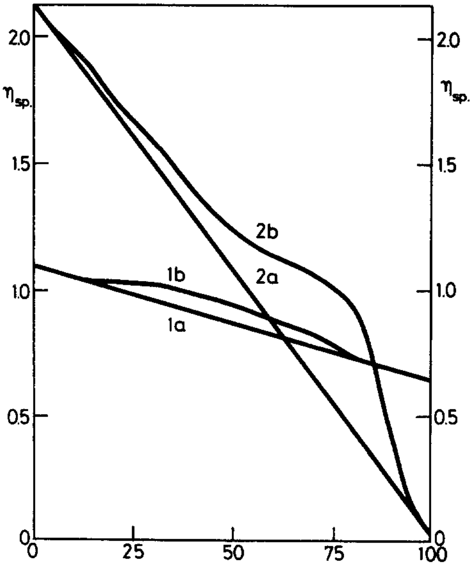


Fig. 1 Dependence of specific viscosity ($\eta_{sp}0.5$ wt.%) of the solution of the polymer-polymer PAA PM-PAN mixture on mixture composition (wt.%). 1a) theoretical additive viscosity curve; 1b) experimental viscosity curve for a composition with PAN-1; 2a) theoretical additive viscosity curve; 2b) experimental viscosity curve for a composition with PAN-2

According to MTA data, the PAN-1 films obtained from DMF do not contain the solvent. This indicates the absence of any strong donor-acceptor interaction between the nitrile group and the DMF molecule.

In the modification of PAN-1, about 50% of acrylonitrile units are transformed into cyclic structures containing imino groups $>C=N-$ and carbonyl groups. According to MTA data (using PAA PM films as an internal standard) the films obtained from a solution of this polymer in DMF contain DMF in an amount of 1/2 mole per elementary unit which corresponds to the ratio of 1 mole of DMF per cyclic structure.

The complexation of PAN-2 with DMF probably occurs as a result of the formation of an H-bond between the imino nitrogen and the DMF hydrogen. The formation of electron donor imine and carbonyl groups resulted that PAN-2 became able to form complexes not only with the solvent but also with carboxylic and amide groups of PAA.

The viscometric investigation of PAA PM-PAN solutions (Fig. 1) show that the interactions between the PAA and PAN-1 molecules are much weaker than for PAA and PAN-2. In fact, for the former system, the deviation of the experimental additive viscosity (curve 1b) of these polymers from the theoretical value (curve 1a) is very slight, whereas for the latter, a strong deviation of the experimental curve (2b) from the theoretical (2a) is observed. As was to be expected, films obtained from a solution of a PAN-1

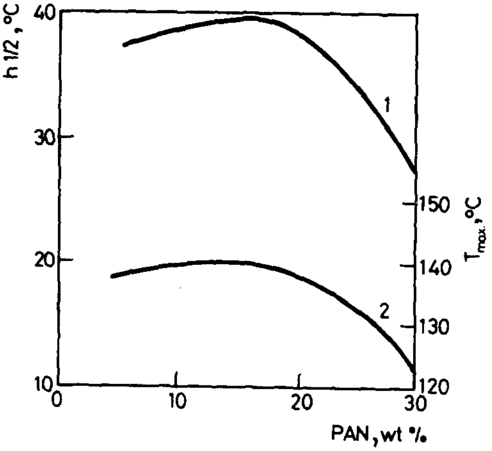


Fig. 2 1) Dependence of halfwidth peak of water elimination ($h_{1/2}$) from PAA PM on PAN-2 content (wt.%) in the composition; 2) Dependence of maximum cyclization temperature (T_{max}) of PAA PM in composition on PAN-2 content (wt.%)

and PAA PM mixture were inhomogeneous and turbid. Homogeneous transparent films were obtained from the solutions of a mixture of PAN-2 and PAA PM in DMF with the content of the former of 5, 10, 15, 20, 25 and 30 weight %. It was established with the aid of MTA that as the concentration of PAN-2 in the composition increases, the peak halfwidth ($h_{1/2}$) of water eliminated in the cyclodehydration of PAA PM decreases. The value of $h_{1/2}$ for PAA PM is about 50°, whereas that for a mixture with 30% PAN-2 decreases to 25° (Fig. 2a). This fact indicates that the set of energetic states of carboxyamide groups after the interaction with cyclic PAN-2 fragments is much narrower than that in the PAA PM film.

The increase in PAN-2 concentration leads to an decrease in the temperature maximum on the curve of the elimination of cyclodehydration water (from 154° for PAA to 122° for a mixture with 30% PAN-2) (Fig. 2b), i.e., the imidization rate increases and the process begins earlier. It may be assumed that as the PAN-2 content increases in comparison to that in the initial PAA, the compositions display on the one hand an increase in morphological homogeneity and on the other a decrease in the mean film density in connection with an increase in the free volume. This facilitates and accelerates the process of imide ring closure. In fact, an independent measurement of composite films by the flotation method showed that the density decreases from 1.350 g/cm^3 for PAA PM to 1.333 g/cm^3 for a composition containing 30% PAN-2 (Fig. 3).

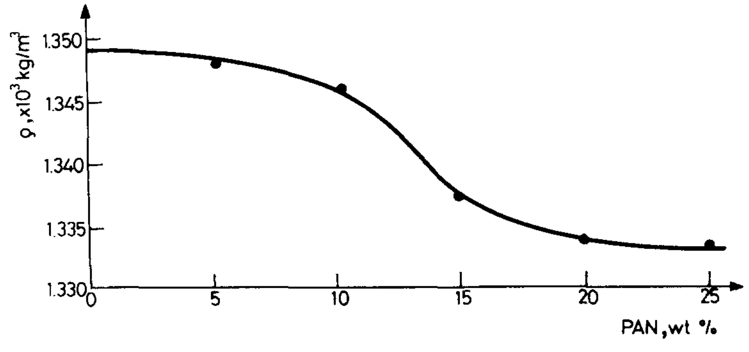


Fig. 3 Dependence of film density (ρ) on content (wt.%) of PAN-2 in the composition

The investigation of the permeability of initial and composite films to gases indicates that the morphologic structure of the investigated materials changes markedly. This is probably expressed in the change of the character

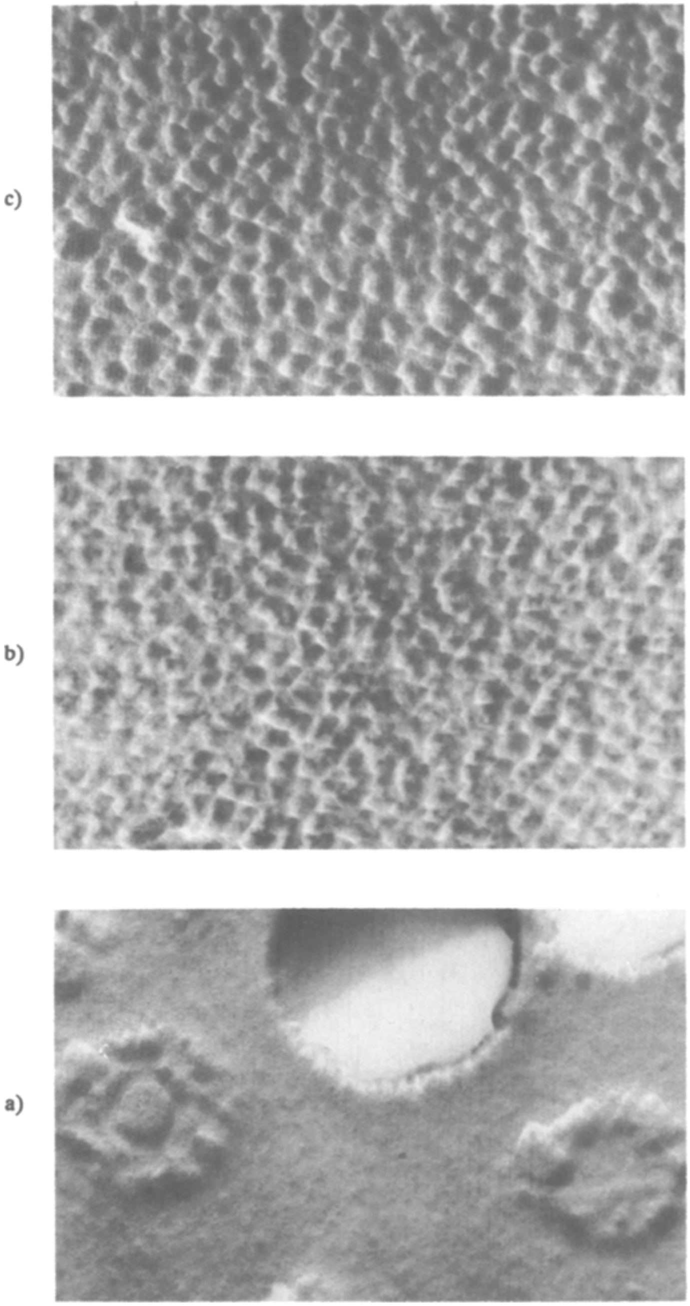


Fig. 4 Microphotographs of single-stage coal-platinum replica from etched free surfaces of composition films of c) PAA PM + 10% PAN-2, b) PAA PM + 25% PAN-2 and a) control PAA PM film

of porosity. The PAA PM films have a permeability coefficient of $P = 1.2.10^{-10}$, with 20% PAN they are impermeable. It may be assumed that in this case "closed" pores predominate, and "open" channels along which gas diffusion occurs are absent. This is confirmed by the data of electron microscopy. Figure 4 shows the microphotographs of one-stage coal-platinum replica from the etched free surfaces of composite films: PAA PM +10% PAN-2 (c), PAA PM + 25% PAN-2 (b) and a control PAA PM film (a). It is clear that films with PAN-2 do not contain ring-shaped associates 0.5-1.0 μm in size regularly filling the PAA PM film.When the percentage of PAN in the composition increases the following facts occur: 1) the size of inhomogeneities (grains) decreases from 70-100 nm at 10% PAN to 40-60 nm at 25% PAN and 2) the surface relief becomes more flat, which shows that the difference in density between the grain and the inter-grain space changes. In other words, the film becomes more homogeneous upon the introduction of up to 30% PAN-2. This also indicates that PAA and PAN interact relatively strongly.

As to the thermal stability of compositions containing from 10 to 40% of PAN (Fig. 5), the TG curves for PAA PM-PAN almost completely agree with that characteristic of PAA PM. In this case the thermal stability of the composition is on the level of the thermal stability of PI.

Table 1 Physico-mechanical characteristics of PI-PM-PAN films

PAN type	Conc. in composition		Young's modulus	Relative elongation	Tensile strength
	PAA PM, %	PAN, %	E, Pa 10^6	ε, σ, %	Pa 10^6
PAN-1	90	10	1540	16	98
	80	20	1422	7.5	88.3
	70	30	1471	5	88.3
	60	40	1177	3	39.23
PAN-2	90	10	1863	21	112.8
	80	20	1961	10	103.0
	control				
	100		1765.2	45	137.3

The results of physico-mechanical investigations are given in Table 1. The absence of interaction between PAN-1 and PAA PM in solution leads to the formation of inhomogeneous films with poor physico-mechanical charac-

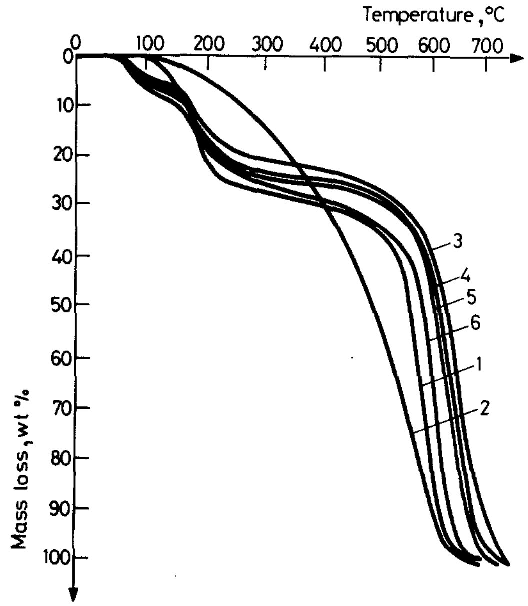


Fig. 5 Thermogravimetric curves of the samples: 1) PAA PM, 2) PAN-2, 3) PAA PM : PAN-2 = 90 : 10 wt.%. 4) PAA PM : PAN-2 = 60 : 40, 5) PAA PM : PAN-2 = 70 : 30, 6) PAA PM : PAN-2 = 80 : 20

teristics with respect to control films from PI PM. Homogeneous films obtained from the solution of a mixture of PAA PM-PAN-2 subjected to imidization were characterized by a slight decrease in tensile strength and by an elastic modulus exceeding the corresponding value for the initial PI PM. This is evidently due to an increase in the ordering of the supermolecular structure of PAA PM in the pressure of PAN-2 as a result of polymer-polymer interaction.

Hence, it was established by the methods of viscometry, MTA and electron microscopy that a strong interpolymer interaction exists between PAA PM and PAN-2.

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The authors express their gratitude to Chalykh A. E. for technical aid and to Kuznetsov Yu. P. for the measurements of permeability of films to gases.

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Zusammenfassung — Polyacrylnitril (PAN) wurde modifiziert, das entstandene Polymer ist (im Gegensatz zu herkömmlichem PAN) ausreichend mischbar mit Polyamicsäure (PAA). PAA, PAN und ihre Gemische wurden in Lösung und als Film mittels Viskosimetrie, massenspektrometrischer Thermoanalyse (MTA), TG und Elektronenmikroskopie untersucht. Die physisch-mechanischen Charakteristika der entsprechenden Verbundstoffilme wurden ermittelt.