Journal of Thermal Analysis, Vol. 36 (1990) 361-376

THERMAL ANALYSIS IN THE INVESTIGATION OF COMPOSITE POLYMERS

Yu. N. Sazanov

INSTITUTE OF MACROMOLECULAR COMPOUNDS OF THE ACADEMY OF SCIENCES OF THE USSR, LENINGRAD, USSR

(Received May 3, 1989)

The methods of thermal analysis are successfully used for identification of the processes of formation, degradation and structurization of composite polymers. On the examples of the investigation of the thermochemical reactions of polyamic acids with polystyrene, polyvinylpyrolidone, polyacrylonitrile, polyvinyltetrazole and epoxy and furol resins, the high yield of information by the methods of thermal analysis in the investigation of these polymers is demonstrated.

At present, there is considerable interest in the problem of the compatibility of various polymers. For the solution of practical problems, it is necessary in many cases to prepare materials whose properties cannot be ensured by one polymer alone. This is particularly so for block and graft copolymers, in the synthesis of which it is possible to combine some opposite characteristics of the initial polymers, e.g. hydrophobicity and hydrophilicity, strength and flexibility, thermoplastic and thermosetting properties, etc. Besides copolymer materials in which elementary fragments or blocks of initial homopolymers are bonded to each other by chemical bonds, there are also composite material in which the homopolymers are joined according to other principles. The deciphering of the mechanism for the formation of composites, and the search for the relationships responsible for the appearance of new qualities of composites differing from those of the initial polymers, is an interesting and feasible problem of thermal analysis. It should be noted that in many cases the formation of composite polymers proceeds at high temperatures, which makes it possible to apply widely all methods of thermal analysis, both in the stage of formation of the

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

composites and in the stages of thermochemical treatment and restructuring of these compounds over a wide temperature range.

The investigation of composite materials is frequently necessary not only for the preparation of new polymers with properties which differ from those of the initial polymers, but also to obtain information about the behavior of some homopolymers operating in close contact each other in various mechanisms and assemblies at temperatures inducting the drastic activation of reactions affecting the thermal stability or heat resistance of the polymer components of the constructions. Under these conditions of operation, the mutual influence of the polymers in direct contact with each other in the zone of high thermal activity is an important factor in the study of thermochemical reactions of composites on the surface level.

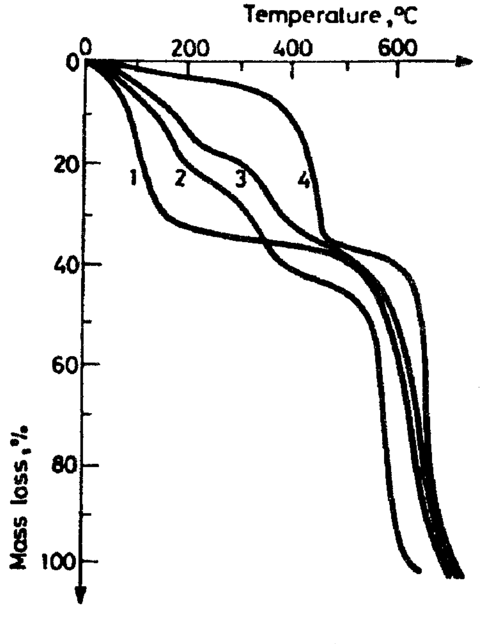


Fig. 1 TG curves of the degradation in air of 1) PAA, 2)PA--PS mechanical blend, 3) PAA--PS block copolymer and 4)PI--PS block copolymer

In the preparation of composites, mixtures are often used in which small amounts of one of the polymers can improve some properties of the other polymer, which forms the main part of the initial mixture. One variant of these materials is the thermally stable composites, in which a polyimide (PI) or its prepolymer, polyamic acid (PPA), play the role of thermostabilizer.

The first work in this field was an attempt to combine PI and polystyrene (PS) in the preparation of block copolymers [1]. In the present work, samples of styrene and PI or PAA were investigated, and for comparison the TG curves of a mechanical blend of PS with PAA and a homo-PAA were considered (Fig. 1). The curves show that the thermal treatment of a mechanical blend of PS with PAA does not increase the thermal stability of PI. It may be presumed that an increased thermal stability of PI will be attained by using PS - PAA block copolymers in which phase separation proceeds on the microlevel rather than the macrolevel.

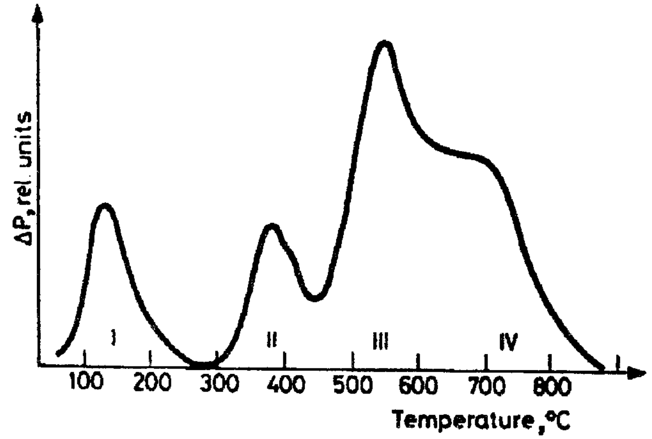


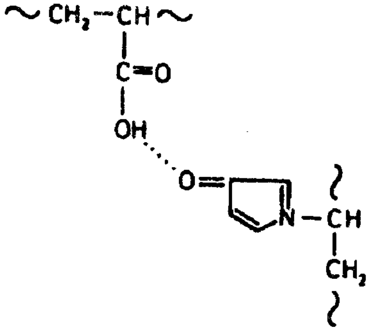
Fig. 2 TVA curves for a PAA--PVP mixture (molar ratio 1 : 1)

In fact, the TG of block copolymers showed that the insertion of PS blocks into the PAA chain leads to an increase in the thermal stability of the block copolymer prepared by thermal imidization. The temperature of the start of thermal degradation of this PI exceeds that of PI obtained in a similar manner by the thermal imidization of homo-PAA. It is possible that styrene blocks undergoing free-radical depolymerization in the same temperature range as that in which the PAA blocks undergo thermal imidization not only decrease the concentration of free radicals in the PI being formed, but also have a plastifying effect, favoring the relaxation of stresses accompanying imidization. In order to confirm the hypothesis that the concentration of free radicals formed in the imidization decreases, the EPR spectra of homo-PAA and block copolymer were taken. The spectra show that at 300-350^o (range of thermal depolymerization of PS) the concentration of radicals in the thermal treatment of homo-PAA is rather high, whereas in the PI formed under the same conditions from the block copolymer, it is close to zero and increases drastically only above 400°, after the degradation of virtually all the PS blocks. Hence, the results of TG, confirmed by spectral investigations, showed that it is possible to increase the thermal stability of PI in the preparation of composites based on it.

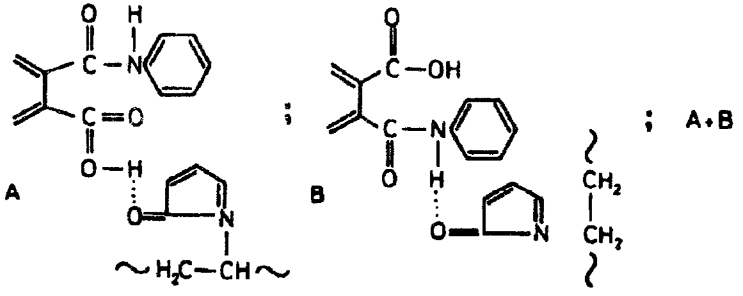
In ref. [2], TVA, pyrolysis gas cromatography and TG were used to investigate the compatibility of PAA with polyvinylpyrrolidone (PVP), which is an interesting polymer for investigating interpolymer interactions on the macromolecular level.

It has previously been established that PAA can form stable complexes with amide solvents, and in particular with N-methylpyrrolide (N-MP) [3, 4]. It is also known that poly-N-vinylpyrrolidone (a high molecular weight analog of N-MP) forms interpolymer complexes with polyacids [5]. It may evidently be expected that an interpolymer complex (ICP) is formed between PAA and poly-N-vinylpyrrolidone.

The interaction between polyacids (polyacrylic, polymethacrylic and other acids) and PVP yields an IPC stabilized by a systems of hydrogen-bonds between the carboxy groups of the polyacid and the carbonyl groups of the pyrrolidone rings [5].



It might be expected that, in general, the interaction between PAA and PVP would occur according to the same principle. However, the ortho-amic acid group, which is a distinguishing feature of aromatic PAA, is characterized by two proton donor centers: a carboxy and an amide group. Moreover, the latter forms hydrogen-bonds no less readily than the former. Hence, it is possible to stabilize the PAA-PVP polycomplex in different ways: with the participation of (A) the carboxy group alone, (B) the amide group alone and (C) both donor groups.



The IPC formed in a solution of PAA and PVP evidently retains the solid phase in a film as a result of cooperative interchain interaction, and determines the course of subsequent intra- and intermolecular reactions.

When PVP is introduced in a molar ratio of 2.0:1.0, water is eliminated in large amounts. This is probably caused by the thermal degradation of PVP present in the system. The presence of water at these very high temperatures leads to the development of thermohydrolytic processes and, as a result, the evolution of large amounts of CO_2 is observed. This is evidently the explanation for the lower thermal stability of the polymer structure in this mixture than in PI alone. Hence, the main differences between the behavior of the samples upon thermal treatment are as follows:

0.5 and 1.0 mole of PVP per mole of PAA	2.0 mole of PVP per mole of PAA
(1) In the cyclodehydration of PAA, interchain bonds are formed with the participation of PVP and amic acid groups of PAA, and the number of imide rings decreases	In the cyclodehydration of PAA, interchain bonds are not formed, and the number of imide rings does not change
(2) No PVP remains in the sample after cyclodehydration (380°C)	0.4 mole of PVP per mole of PI remains after cyclodehydration

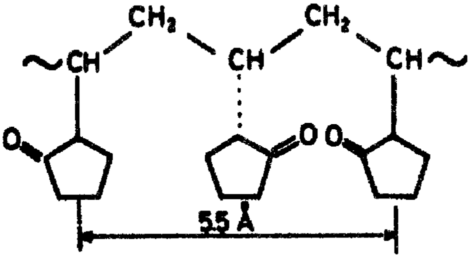
These differences clearly indicate that the mechanism of polymer interaction is affected by the composition of the mixtures.

This fact may be interpreted as follows.

The formation of an IPC is usually possible if the macromolecules participating in it are complementary. Chemical and structural complementarities are distinguished [6]. In most cases, IPCs are formed as a result of the chemical complementarity of the interacting macromolecules. This type of IPC between PAA and PVP has been described above and probably exists at PVP/PAA ratios of 0.5:1.0 or 1.0:1.0.

In the formation of an IPC, one type of macromolecule behaves as the matrix and the other type as the side "daughter" chains. This assignment is evidently tentative and depends on many factors, including the quantitative ratio of the components. We believe that at the above PVP/PAA ratios the macromolecule of PAA plays the part of the matrix, whereas the chains are attached to the matrix by analogy with a "lightning fastener". However, beginning from a certain ("critical") value of the PVP:PAA ratio (according to our data, this value is approximately 2:1), the types of interaction between the IPC components change. The macromolecules of PVP now play the part of the matrix, and those of PAA become the side ("daughter") chains.

The intramolecular cyclodehydration of PAA is correspondingly facilitated, and linear PI chains are formed (as observed experimentally). Furthermore, in this case the possibility of the formation of the PI-PVP complex arises, as a result of structural complementary. This has been realized, as shown experimentally. In fact, in the formation of the supermolecular structure of PI, layer chain packing appears and the "parquet" structure is formed. In this structure the interplanar distance is close to 5.5 Å. The pyrrolidone rings (if alternate rings are counted) are located at the same distance [7]:



The transverse dimensions of the pyrrolidone and the imide rings are also close to each other, which suggests the following structure of IPC (Fig. 3).

The stabilization of the complex, as in the ordered PI structure, is due to the dipole-dipole interaction between the carbonyl groups of neighboring chains [8]. However, the pyrrolidone ring contains only one carbonyl group and, hence, the interaction in the IPC is slightly weaker than in pure PI. Nevertheless, this interaction ensures the existence of the IPC up to very high temperatures (380°). In the IPC pyrolysis, the PVC macromolecules are the first to undergo degradation (as was to be expected). After PVP is

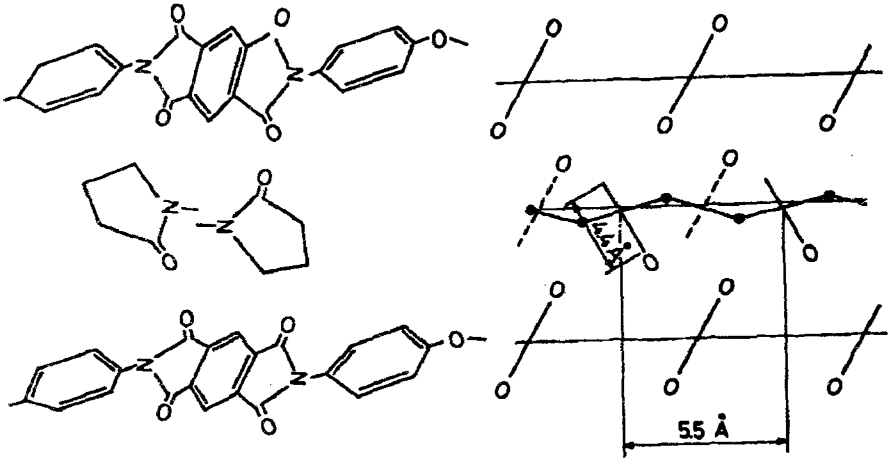


Fig. 3 Scheme for the suggested structure of PI--PVP composite

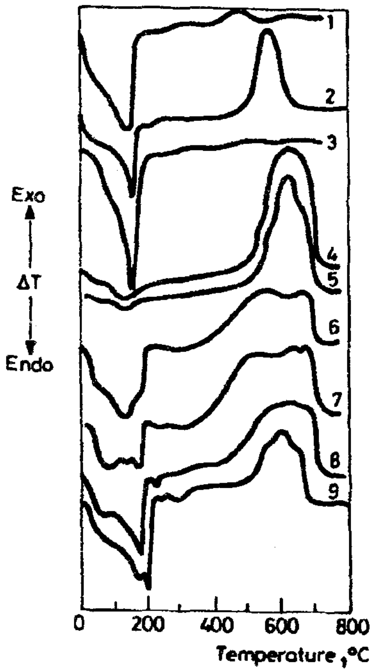


Fig. 4 DTA curves of samples 1-9 (Table 1)

eliminated from the sample, the supermolecular structure of PI is characterized by a great number of defects, and as a result the thermal stability decreases slightly. As to the fate of the "extra" pyrrolidone ring in the PVP molecule, it might be suggested that this ring is either located in the IPC on the other side of the aliphatic chain, as a result of the bending distortions of this chain induced by the requirements of the minimum free energy of the IPC or is eliminated during formation of the IPC at 200-300°, which is usual for PVP.

Other composites used for thermoanalytical investigations were composite polymers based on PAA and furfuryl alcohol (FA) [9]. In the analysis of a number of mixtures of initial reagents (Table 1), interpolymer interaction between them was revealed at high temperatures (Figs 4 and 5). When infrared spectroscopy and ^{13}C NMR data is a solid body were compared, conclusions were drawn on the mechanism of composite formation.

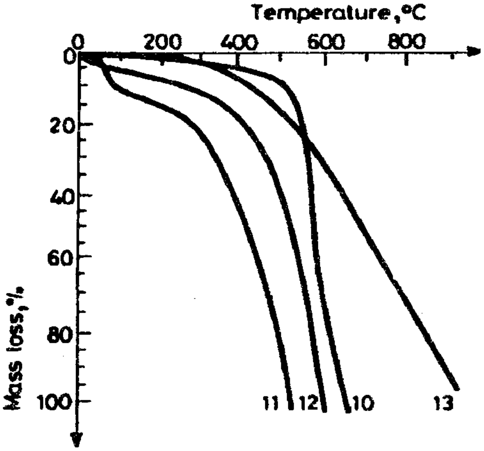
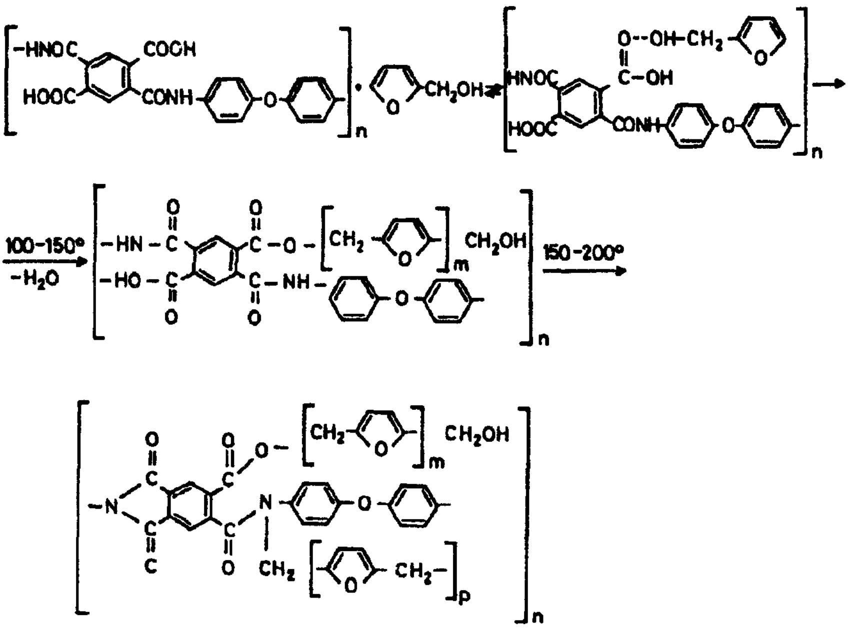


Fig. 5 TG curves of samples 10-13 (Table 1)

The second component was chosen because furan resins are widely used in industry [5]. Thus, it is known that the introduction of FA into the composition of carbon articles with subsequent condensation can result in an improvment of such properties as strength, gas impermeability, chemical resistance and antifriction [6]. The purpose of this paper is to determine the conditions and character of the reactions between the components of the PAA-FA system.



The interaction was investigated by DTA at a heating rate of 2.3 deg min^{-1} in air, in ceramic crucibles. The reaction products were investigated by IR and high-resulution NMR spectroscopy and TG.

When the PAA-FA composition is heated, PAA is the initiator of the polymerization of FA, and the interaction between the components is profoundly affected by their ratio and by the temperature and duration of treatment. One of the variants of a possible interaction between the initial components at the PAA:FA ratio of 25:75, on heating at 250° for 2 h, can be represented by the following scheme:

a) When FA is added to PAA at room temperature or with slight heating, hydrogen-bonds are formed between the hydroxy groups of FA and the carboxyl groups of PAA.

b) Heating of the resulting mixture up to 100-150° leads both to the polymerization of FA and to interaction between one of the carboxyl groups of PAA and the hydroxy end-group of FA, with formation of an ester bond.

c) Upon further heating of the mixture to 150-200°, PAA undergoes cyclodehydration, and intermolecular bonding of the amide group of PI to the hydroxy group of FA takes place.

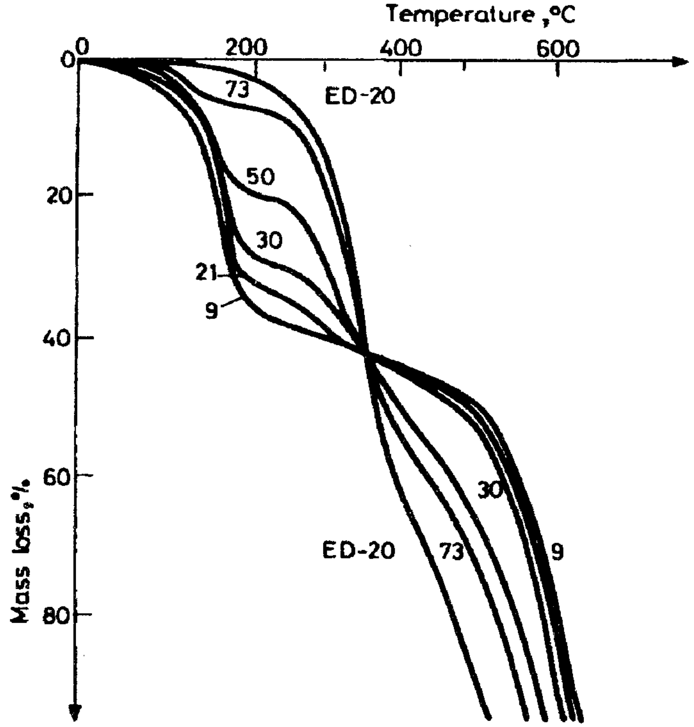


Fig. 6 TG curves of PAA--epoxy resin (ED--20) mixtures. The data on the curves denote the resin content

The calculated values of the elemental composition for this final product are in approximate agreement with those determined for the product of interaction between PAA and FA. Thus, calculation of the percentage of nitrogen showed that the resulting structure contains one elementary PI unit per 2.75 FA units.

Bearing this scheme in mind, it should be taken into account that, when the PAA-FA mixture is heated, besides the above reactions other reactions will also occur, for example the dissociation of the PAA-solvent complex or cross-linking reactions with the formation of cross-linked structures. Higher temperatures of heating of the mixture will lead to the formation of bonds as a result of opening of the five-membered FA rings.

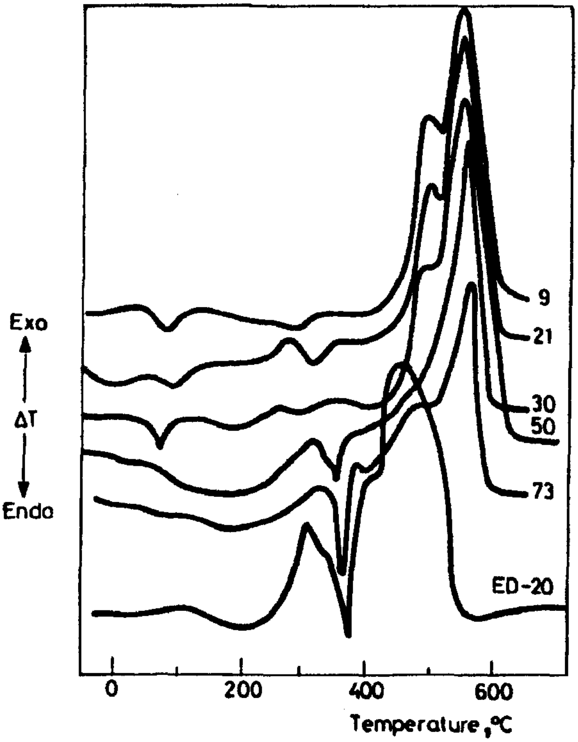


Fig. 7 DTA curves of PAA--epoxy resin (ED-20) mixtures. For symbols, see Fig. 6

This TG study of the compatibility of PAA with epoxy resins having different ratios of initial components shows that for this pair too the methods of thermal analysis reveal the changes arising upon the thermal treatment of these mixtures. Two ranges may be distinguished from comparisons of the TG curves (Fig. 6). The first is the range 20-330°, in which the thermal stability of the composite is determined by the temperature parameters of the epoxy resin. In this temperature range, the resin begins to degrade at about 200°, and at 300° the mass loss is about 40-50%. As for PAA, the imidization is terminated at 200°, and at 330° the last traces of the complexed solvent and water are removed (the mass loss from 200 to 330° is about 5-7%).

The second thermal stability range is determined by the temperature parameters of the more thermally stable PI and the PI-epoxy resin ratio. No specific features peculiar to the composite are observed in the TG curves. However, for the DTA curves (Fig. 7), and in particular when the mixtures

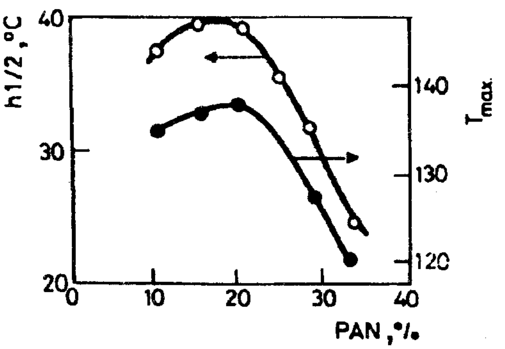


Fig. 8 Kinetic characteristics of PAA imidization in PAN solution vs. PAN concentration

are compared with pure ED-20 resin, a considerable exothermic peak is observed in the temperature range 380-540° for the resin, which is absent for the mixtures. At first sight, this effect suggest that, when the mixtures are heated under the experimental conditions, PAA interacts with the epoxy resin in this temperature range.

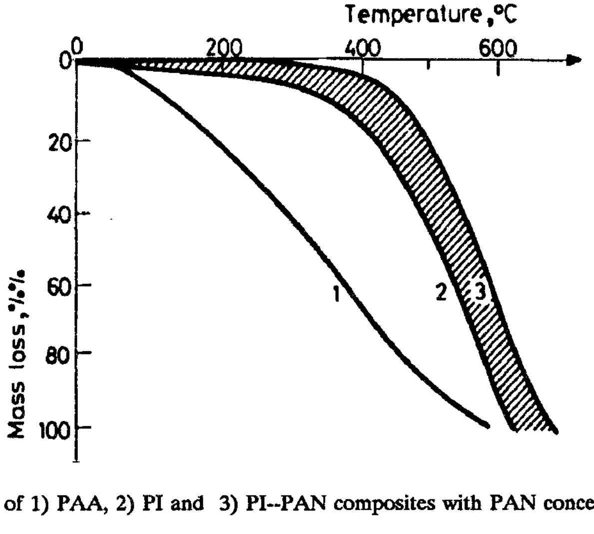


Fig. 9 TG curves of 1) PAA, 2) PI and 3) PI--PAN composites with PAN concentration from 10 to 35%

In conclusion, it should be noted that PAA composites with polyacrylonitrile (PAN) and polyvinyltetrazole (PVT), which contain nitrogen atoms in the side-chain, are interesting composites for the study of the compatibility of PAA with other polymers. They are interesting from the

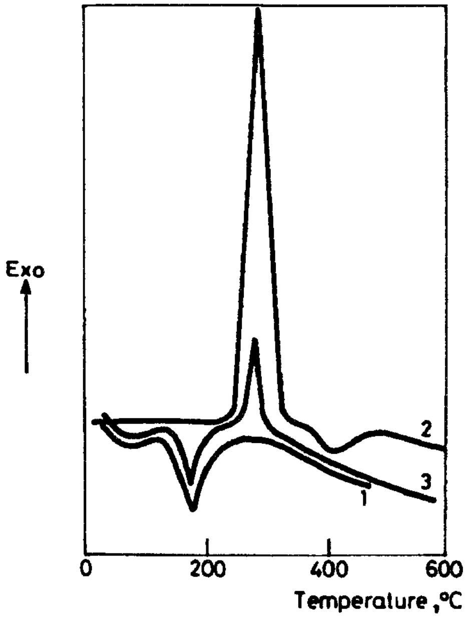


Fig. 10 DSC curves of 1) PAA, 2) PVT and 3) PAA--PVT mixture (7 ; 3)

viewpoint of the processes of thermochemical reactions leading to the formation (in the case of PAA) or degradation (in the case of PVT) of nitrogen-containing heterocycles which are coplanar structural components to the benzimide ring of PI and play a certain role in the carbonization of thermally stable polymers.

The thermal analysis of mixtures of PAA with PAN showed that composite polymers based on them are formed only when PAA is mixed with a partially cyclized PAN. In contrast, linear PAN is incompatible with PAA, although both polymers are well soluble in DMF. When PAA interacts with cyclic PAN, a composite is formed [10], the thermal properties of which differ from those of the initial components. Thus, in Fig. 8 the mass-spectrometric thermal analysis data show that the introduction of PAN into a solution of PAA essentially changes the kinetic parameters (the temperature of maximum water evolution in the cyclization of PAA, and the half-width of the water peak according to the MTA curves) of thermal cyclodehydration of PAA. When TG was carried out on composite polymers obtained from mixtures of PAA and PAN, with subsequent thermal treatment at 50-200°, at a heating rate of 5 deg/min, it was found that, although

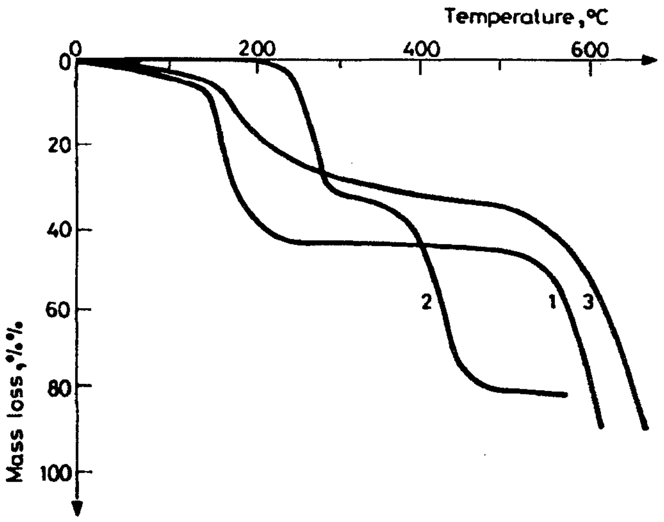


Fig. 11 TG curves of 1) PAA, 2) PVT and 3) PAA--PVT mixture (7 : 3)

the content of PAN in the composite increased, its thermal stability was determined by the thermal parameters of PI, i.e. the most thermally stable component in it (Fig. 9)

Sample no.	Composition, and nature of sample
1	FA, liquid
2	13% PAA in DMAA
3	50% FA + 50% DMAA, mixture
4	Film prepared from a mixture of 47% PAA + 53% FA
5	PAA film
6	0.6% PAA (13% solution in DMAA) + 99.4% FA
7	9% PAA (13% solution in DMAA) + 91% FA
8	20% PAA (13% solution in DMAA) + 80% FA
9	47% PAA (13% solution in DMAA) + 53% FA
10	PI, powder heated at 400° for 3 h
11	PFA, powder obtained by heating FA at 300° for 2 h
12	25% PI powder + 75% PFA powder, N content 4.3%
13	25% PAA (13% solution in DMAA) + 75% FA, N content 4.3%, heated at 250° for 2 h

The numbers in the Table correspond to the numbers of the curves in the Figures

Hence, the PI component of the composite exerts a stabilizing effect on the entire composite, preventing the occurrence of thermo-oxidative degradation.

If one judges from the appearance of the DSC curves (Fig. 10), there is no interaction between PAA and PVT in their mixtures. Curve 3 distinctly shows the endothermic effect of PAA cyclization and the exothermic effect of the breaking of the tetrazole ring. However, the quantitative characteristic of this effects differ from those in the cyclization of homo-PAA and the thermal degradation of PVT. Thus, the heat absorption value for the first effect decreases from 131 to 91.3 J/g, while for the second effect the amount of heat evolved decreases almost 6-fold, from 841 to 144 J/g. These data shows that both polymers appreciably affect the specific thermochemical reactions proceeding when their mixtures are heated. This conclusion is supported by the TG data for the same polymers (Fig. 11). It can be seen from these data that the kinetics of thermal degradation of the PAA-PVT mixture essentially reveal the thermal degradation of the composite, which exhibits the synergetic effect of increasing the thermal stability of both PI and PVT.

Hence, the methods of thermal analysis may be used for very effective investigations of the mechanism of formation of composite polymers and evaluation of their thermal characteristics.

References

1 M. M. Koton, V. N. Artemeva, N. V. Kukarkina, L. M. Scherbakova, Yu. N. Sazanov, G. N. Fedorova and N. L. Ushakova, Visokomol, Soed., 26B, (1984) (11) 830-832.
2 Yu. N. Sazanov, T. Székely, T. A. Antonova, E. Jakab, M. Blazso, S. A. Dauengauer, L. A. Shibaev and T. N. Spirina, Thermochim. Acta., 102 (1986) 223-238.
3 Yu. N. Sazanov, L. A. Shibaev, T. I. Zhukova, N. G. Stepanov, S. A. Dauengauer and T. M. Bulina, J. Thermal Anal., 27 (2) (1983) 333-341.
4 Yu. N. Sazanov, L. A. Shibaev, T. I. Zhukova, S. A. Dauengauer, N. G. Stepanov, T. M. Bulina and M. M. Koton, Dokl. Acad. Nauk SSSR, 265 (4) (1982) 917-920.
5 V. A. Kabanov and I. M. Papisov, Vysokomol. Soed., 21A (1979) 243-249.
6 A. A. Litmanovich, S. V. Markov and I. M. Papisov, Dokl. Acad. Nauk SSSR, 278 (3) (1984) 676-681.
7 P. Behmel and C. Weber, J. Mol. Struct. 116 (3-4) (1983) 271-275.
8 V. A. Zubkov, A. V. Sidorovich and Yu. G. Baklagina, Vysokomol. Soed., 22 A (12) (1980) 2706-2711.
9 I. E. Simanovich, G. N. Fedorova, N. V. Mikhailova, A. S. Bobasheva, A. V. Gribanov and Yu. N. Sazanov, J. Thermal Anal., 34 (1988) 289-295.
10 T. N. Spirina, A. V. Novoselova, T. E. Suchanova, V. N. Zgonik and Yu. N. Sazanov, Vysokomol. Soed., in press.

Zusammenfassung - Thermoanalysenverfahren sind bei der Erkennung der Prozesse von Bildung, Abbau und Strukturisierung von Mischpolymeren äußerst nutzvoll angewendet worden. Die hohe Informativität dieser Methoden bei der Untersuchung von Polymeren wird am

Beispiel der Untersuchung der thermochemischen Reaktion von Polysäuren mit Polystyren, Polyvinylpyrrolidon, Polyacrylnitril, Polyvinyltetrazol sowie Epoxy- und Furolharzen verdeutlicht.