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THERMOCHEMISTRY OF POLYMERS BASED ON VANILLIC ACID

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Abstract

Thermal analysis of polyester and polyamides based on vanillic acid derivative – terephthaloyl-bis-(3-methoxy-4-oxy benzoic) acid has been reported. Different behaviours with the appearance of the thermal degradation, stucturization and carbonization stages were detected.

Thermochemical behaviour of polymers under investigation revealed that technical lignin derivative – vanillic acid are a promise for obtaining polymer materials with good properties.

Keywords: polyamides, polyesters, technical lignin, thermal analysis, vanillic acid

Introduction

Technical lignin is one of the main by-products of chemical wood processing. Lignin can be converted to compounds such as vanillin, vanillic acid, syring aldehyde, phenol pyrocatechin, etc. [1, 2]. Of particular interest among them is vanillic (3-methoxy-4-hydroxybenzoic) acid, for the synthesis of polyesters with mesogenic groups in the main polymer chain. The properties of a number of polyesters based on *p*-hydroxybenzoic acid and its derivatives have been described in the literature [3–6]. These polyesters are usually liquid-crystalline systems with good mechanical properties and satisfactory thermal stability. The use of vanillic acid in their synthesis renders them soluble and fusible, which improves their technologic properties when they are processed into finished products [7]. The interest in polyamides based on vanillic acid is due to the application of lignin hydrolysis products not only for the synthesis of polyamides as such, i.e. for extending the range of polymer materials, but also for the preparation of thermally stable binders and impregnating systems with a high adhesion stability with respect to technical tissues based on man-made fibers.

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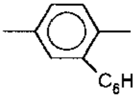
For brevity, polyesters and polyamides based on vanillic acid will be called PEs and PAs, respectively; the acid component of these polymers is based on terephthaloyl-bis(3-methoxy-4-hydroxybenzoic) acid (TBA), the synthesis of which has already been described [7]. To obtain PEs, aliphatic and aromatic diols were used with the general formula HO–A–OH, where A is

$—(CH_2)_6—$ (PE-1); $—(CH_2)_{10}—$ (PE-2);

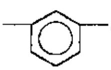
(PE-3);

or

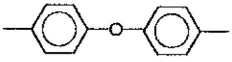


(PE-4).

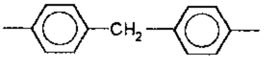
To obtain PAs, aromatic diamines were used with the general formula $H_2N–B–NH_2$, where B is



(PA-1);



(PA-2);



(PA-3);

(PA-4)

All these polymers are well soluble in aprotic organic solvents and melt below the temperature of the start of degradation of the main chain.

Results and discussion

As expected, the comparison of the TG curves of these PEs revealed a regular relationship between the structure of the diol and the thermal stability of the polymer.

The general pattern of thermal degradation of the PEs is characterized by three stages [Fig. 1]. In the first stage, when a polymer sample is heated at a linear heating rate, volatile products weakly bound to the sample are removed. They are usually sorbed residues of the solvent and moisture. In this stage, the absolute mass loss of the samples is 2–5% and does not depend on the PE structure. At temperatures above 320–350°C, intensive PE degradation begins, with the formation of a large amount of volatile products of thermal and thermooxidative degradation. The quantitative parameters of this process depend on the chemical structure of the diol component. Thus, the degradation of PEs based on aliphatic diols is characterized by high mass loss rates of about 10% min^{-1} in the temperature range from 350 to 420°C and an overall mass loss of 70–75% whereas the PEs based on aromatic diols exhibit a lower degradation rate, and their mass loss at 500°C is about 50%. For the aromatic PEs, the third degradation stage begins from 440°C, with a considerable decrease in the quantity of volatile products isolated. By 800°C, PEs with aliphatic diol fragments have burned away almost completely.

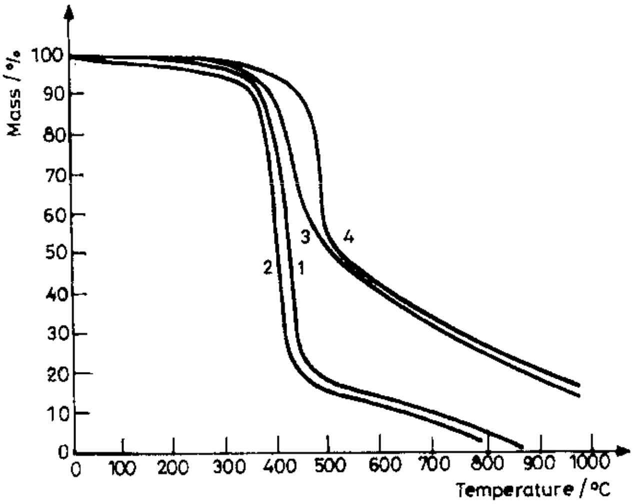


Fig. 1 TG curves of PE: 1 – PE-1, 2 – PE-2, 3 – PE-3, 4 – PE-4

For PEs with aromatic substituents, the amount of carbonized residue is 23–30%. In this case, the phenyl substituent in the nucleus of the aromatic diol exerts an effect. This substituent is evidently responsible for the highest value of T_o=380°C among the PEs investigated. As concerns the mechanism of PE thermal degradation, in the stage of intensive degradation the predominant reactions (as shown by the examples of other polyesters [8–10]) are decarboxylation and decarbonylation of the ester groups which determine the main chain structure. The absolute mass losses in the intensive degradation stage can be compared with the relative carbonyl and ester group contents in the PE elementary unit and with the methylene unit contents in the PEs based on aliphatic diols.

Table 1 gives the calculated percentages of thermolabile groups in the PEs under investigation and the actual mass losses in the intensive degradation stage.

Comparison of these data demonstrates that the thermal degradation reactions involving CO and CO_2 evolution predominate in the thermochemical process of degradation of PEs based on aromatic diols. It is quite probable that some hydroxymethylene groups remain in the polymer up to relatively high temperatures and participate in the formation of intermolecular cross-links at the start of carbonization. For PEs with aliphatic groups, the mass loss data in the second stage coincide almost fully with the calculated values for all thermolabile groups in the PE.

In the final thermal degradation stage, the mass loss rate decreases considerably, which indicates that the contribution of structurization reactions with the formation of carbonized products increases. PEs enriched with aromatic units give a greater amount of carbonizate than do PEs with aliphatic units. In this stage, the PE mass loss rate has a linear character and is about 0.3–0.4% min^{-1} for

Table 1 Contents of thermolabile groups in PEs

PE index	Quantity of thermolabile groups/ %				Total quantity of thermolabile groups/ %	Mass loss in the second stage/ %
	CO	CO_2	$-OCH_3$	$-(CH_2)_4-$		
PE-1	20.4	32.8	11.6	15.7	80.5	15.8
PE-2	18.5	29.1	10.3	23.2	81.1	19.0
PE-3	20.1	32.4	11.5	–	64.6	52.2
PE-4	18.2	28.6	10.0	–	56.8	50.0

aliphatic PEs and 0.8–1% min^{-1} for aromatic PEs. These data show that carbonized residues exhibit low thermal stability and upon further temperature rise continue to degrade with the formation of volatile products. The carbonizate structure is based on the TBA unit and aromatic diol fragments. However, as the initial PEs have a high oxygen content and also contain flexible aliphatic sequences, the carbonizates undergo further decomposition, losing heteroatoms and hydrogen, leading to gradual burning away of the entire polymer at 800 and 1000°C for aliphatic and aromatic PEs, respectively.

As concerns the character of PA thermal degradation (Fig. 2), PA based on vanillic acid and *m*-phenylenediamine may be used as a typical example. TGA revealed that its thermal degradation up to 1000 °C proceeds in four stages. In the first stage, from room temperature up to 150–200°C, low molecular mass products (usually residues of sorbed water and solvent) are gradually evolved (about 3%). In the temperature range 135–140°C, the sample undergoes softening, reflected in a characteristic change in the DTA curve shape. In the second stage,

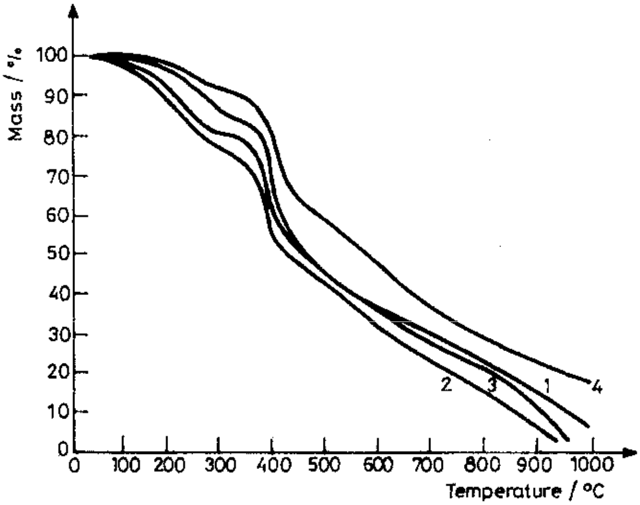


Fig. 2 TG curves of PA: 1 – PA-1, 2 – PA-2, 3 – PA-3, 4 – PA-4

from 100 to 340°C, the mass loss increases considerably up to 250°C (the absolute mass loss rate in this range is abut 7%), and subsequently the TG curve becomes flatter up to 330°C. From the energy viewpoint, this stage is characterized by a smooth increase in heat evolution, with a maximum at 338°C. This effect can be explained by the competition of the reactions of degradation and structurization at the amide groups, which is characteristic of PAs. However, a further change in mass loss, related to structurization at the amide groups, is suppressed by ester group degradation. At temperatures above 325°C, decarboxylation and decarbonylation of ester groups takes place, as shown above for PEs. Beginning from 330°C, the thermal degradation rate increases drastically, with a maximum at 379°C. The third thermal degradation stage, ranging from 330 to 430°C, is characterized by a total mass loss of 32%, with a maximum rate of 4.4% min^{-1}. The thermal effects accompanying the third stage are reflected by the superposition of several maxima, with a predominance of endothermic processes. This is probably caused by the intensive evolution of a number of low molecular mass products of main chain degradation involving decarboxylation. However, at the same time structurization reactions take place in the direction of total carbonization of partially degraded macromolecules which are deprived of a considerable proportion of their heteroatoms. A comparison of the fraction of heteroatoms and their volatile compounds in PA-1 (Table 2) with the mass losses in the range of intensive thermal degradation permits some suggestions concerning the degradation mechanism in the third stage. If it is assumed that, by the end of the third stage, i.e. by 430°C, no heteroatoms remain in the polymer, the coincidence with the mass loss in the third stage is complete. Nevertheless, numerous literature data and our own experience with polyheteroarylene degradation indicate that some heteroatoms (in particular nitrogen, the content of which in this PA is 5.2%) still remain in the carbonized residue up to 1000°C and higher. Hence, it is more probable that water and oxides of carbon are the principal volatile products in the third stage. Their total quantity can amount to 30–33%, which is most probable taking into account the contribution of thermooxidative processes.

The fourth stage is characterized by a slow monotonous loss in mass, which is 70% at 700°C. In this stage, further carbonization occurs with the elimination of some of the remaining heteroatoms and hydrogen atoms, and also some of the carbon atoms, removed in the form of low molecular mass hydrocarbons or as a result of probable cross-linking.

If the parameters of PA degradation are compared with those of the degradation of PEs with similar structures, it is clear that the thermal stability of the PEs is higher than that of the PAs, mainly because the thermal degradation mechanism is more complex due to the presence of the amide bond in the polymer chain. This suggests that the breaking of the amide bond, which is usual in the thermal degradation of PAs, initiates thermohydrolytic reactions competing with structurization reactions. However, these processes are of a local character with respect to temperature and have no marked effect on the subsequent PA carbonization stage, the general profile of which is similar to that of PE carbonization.

Table 2 Calculated quantities of heteroatoms and volatile compounds based on them in PA-1

No.	Heteroatoms and volatile compounds/%						
	O	N	CO	CO_2	H_2O	NH_3	$(CH_3)_2O$
1	26.0	5.0	35.3	31.8	22.7	6.1	16.6
2	–	–	20.2	28.3	6.5	3.0	8.4

1 – maximum possible evolution of volatile products,
2 – optimum evolution of volatile products in the temprature range from 330 to 430°C

It may be observed in the analysis of TG curves of other PAs that the use of aromatic diamines with a swivel between phenyl nuclei, i.e. of the methylene and ether groups, does not change the four-stage character of PA thermal degradation. The difference can be seen only in the first and second degradation stages, which are characterized by greater mass loss for PAs based on *m*-phenylenediamine. This is evidently caused by the greater flexibility of PA molecules with swivel groups in the diamine component. As for PA samples which contain rigid microblocks of consecutively bound phenyl and 2.5-pyrimidine fragments, the increase in their thermal stability with respect to all temperature – mass parameters as compared with other PAs reflects the effects of the concentration of aromatic units in the PA chain.

Conclusions

The thermochemical transformations of the studied polyesters and polyamides based on vanillic acid derivatives revealed that semiproducts of chemical wood processing are of promise for obtaining polymers with relatively high thermal stability, solubility and fusibility.

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