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Thermal Decomposition and Combustion of γ -irradiated Polyamide 6 Containing Phosphorus Oxynitride or Phospham

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Abstract

Polyamide 6 (PA-6) containing the fire retardants phosphorus oxynitride ((PON)_m) or phospham ((PN₂H)_n) was exposed to ⁶⁰Co-γ-rays (absorbed dose: 1.0–4.0 MGy). The irradiation led to crosslinking of the polymer which caused an increase in the char yield and a decrease in the flammability of the polymer. The combustion behavior was strongly affected by irradiation: dripping was totally prevented in the case of system PA-6/(PN₂H)_n and strongly retarded in the case of system PA-6/(PON)_m. The thermal stability of the system PA-6/(PN₂H)_n decreased with increasing absorbed dose whereas the thermal stability of the system PA-6/(PON)_m did not change.

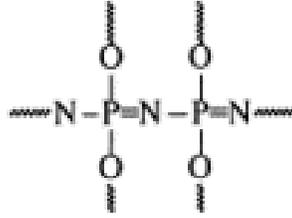
1. Introduction

In our earlier work^[1] we studied the influence of high energy irradiation on the thermal stability of polyamide 6. It was shown that irradiated polyamide shows volatilisation at lower temperature than the unirradiated polymer because of the presence of low molecular weight material generated by radiation-induced chain scission. Apart from chain scission, irradiation also produces intermolecular cross-links and this leads to increased char formation when the irradiated polyamide is heated to 600°C. However, in contrast to the expectation, in this case the enhancement in the char yield is not connected to a decrease in the flammability of the polymer. This might be due to the fact that the amount of char is not high enough to cause fire retardancy^[2]. Generally, an increase in the char yield is attainable with the aid of crosslinking-accelerating additives. For example, it was shown^[1] that phospham, a phosphorus nitrogen polymer, accelerates radiation-induced crosslinking of polyamide 6 more efficiently than triallylcyanurate, a commercial crosslinking enhancer, and that polyamide 6 crosslinked by ⁶⁰Co-γ-rays and containing phospham exhibited relatively extensive charring^[1].

In this work, new results concerning the influence of ⁶⁰Co-γ-irradiation on the charring and combustion performance of polyamide 6 containing phospham or phosphorus oxynitride are presented. These compounds are known to be effective fire retardants for aliphatic polyamides^{3, 4}.

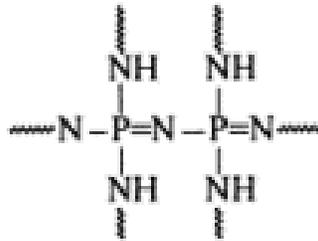
2. Experimental part

A commercial polyamide 6 (PA-6, product of Khimvolokno, Grodno, $M_n=3.5 \times 10^4 \text{ g mol}^{-1}$) was used.



Phosphorus oxynitride $(PON)_m$ of the hypothetical structure

was prepared according to the method suggested by Sommer^[5]. Urea, melamine and phosphoric acid (85% water solution) were mixed at the ratio 30 : 1 : 8 and heated in an oven for 1 h at 120°C and then for 1.5–2.0 h at 350°C. The cooled white mass was finely powdered and heated again in a stream of dried air at 750°C for 2 h.



The imide analog of $(PON)_m$, phospham $(PN_2H)_n$ was prepared by heating in vacuum at 300°C for 2.0–3.0 h of hexaaminotricyclophospazene^[6].

PA-6 was mixed at a 20% wt level with $(PN_2H)_n$ or $(PON)_m$ in a closed mixer operated for 5 min at 60 rpm at 240°C. Bar specimens (6 × 3 × 120 mm) for combustion tests were cut from slabs prepared by compression molding at 250°C. The specimens were irradiated under argon with ⁶⁰Co-γ-rays at an absorbed dose rate $Dr_{abs}=2.6$ kGy/h.

Combustion tests were performed according to the ASTM D 2863 standard limited oxygen index (LOI) test. In this test the lowest limit of oxygen concentration in nitrogen/oxygen mixtures capable of sustaining candle-like combustion of vertically positioned polymer specimens is determined^[7]. The samples were burned from the top and the char formed on top of the self-extinguished specimens was separated and weighted (w_{char}). The char yield was then obtained according to [Eq. \(1\)](#)

$$\text{Char Yield}(\%) = w_{char} / (w_{inr} - w_{resid.}) \quad (1)$$

Here, w_{inr} and $w_{resid.}$ denote the sample weight before and after burning, respectively. Horizontally positioned specimens were ignited in air to check the tendency of the samples to produce flaming drips. Thermal analysis was carried out under a flow of nitrogen or air (60 cm³/min) at a heating rate 10°C/min by using a Mettler thermal analyzer TA 3000.

3. Results and discussion

(a) *Solubility tests*: Irradiated samples containing either $(\text{PN}_2\text{H})_n$ or $(\text{PON})_m$ are insoluble in sulfuric acid even at the lowest absorbed dose (1.0 MGy), which indicates that the polymer is efficiently intermolecularly crosslinked upon irradiation with ^{60}Co - γ -rays.

(b) *Combustion tests*: It is seen from [Table 1](#) that in the case of system PA-6/ $(\text{PN}_2\text{H})_n$ the LOI grows from 29 for the unirradiated formulation to 33 for the formulation exposed to 3.0 MGy. Prolonged irradiation to 4.0 MGy causes a decrease to LOI=32.

Table 1. Effect of absorbed dose on limiting oxygen index and char yield

Additive	Absorbed dose (MGy)	LOI	Char yield (%)
$(\text{PN}_2\text{H})_n$	0	29	22
	2.5	32	
	3.0	33	25
	4.0	32	27
$(\text{PON})_m$	0	28	33
	1.0	27	29
	2.0	31	34
	3.0	31	44
	4.0	33	40

In the case of system PA-6/ $(\text{PON})_m$ the LOI decreases at low irradiation dose (1.0 MGy) but increases at higher doses and reaches LOI=33 at 4.0 MGy which is definitely higher than LOI=28 found for the unirradiated sample. From these results it is concluded that the fire retardancy of both systems is increased by irradiation with ^{60}Co - γ -rays.

Both systems, PA-6/ $(\text{PN}_2\text{H})_n$ and PA-6/ $(\text{PON})_m$ exhibit a tendency to produce more char with increasing absorbed dose. This trend seems to be interrupted in the case of system PA-6/ $(\text{PON})_m$ at $D_{\text{abs}}=1$ MGy, where the char yield is lower than for the unirradiated sample.

Upon combustion in air unirradiated samples of both systems formed flaming drips but self-extinguished in the case of $(\text{PN}_2\text{H})_n$ within 10 s and in the case of $(\text{PON})_m$ within 30 s. When irradiated samples were tested, it turned out that they also self-extinguished within 10 and 30 s, respectively but flaming drips were not formed at all in the case of system PA-6/ $(\text{PN}_2\text{H})_n$ and in the case of system PA-6/ $(\text{PON})_m$ flaming drips were formed with a rate reduced by the factor 5 compared to the unirradiated sample. Obviously, radiation-induced crosslinking totally prevents dripping during combustion in the case of $(\text{PN}_2\text{H})_n$, and it retards dripping significantly in the case of $(\text{PON})_m$.

(c) *Thermal gravimetric analysis*: TGA curves recorded with unirradiated and irradiated samples of system PA-6/ $(\text{PN}_2\text{H})_n$ under argon or air are shown in [Fig. 1](#) and [Fig. 2](#),

respectively. Analogous results obtained with the system PA-6/(PON)_m are shown in [Fig. 3](#) and [Fig. 4](#). The temperatures corresponding to 5% and 10% weight loss and the solid residue fractions measured at 450°C and 600°C are compiled in [Table 2](#).

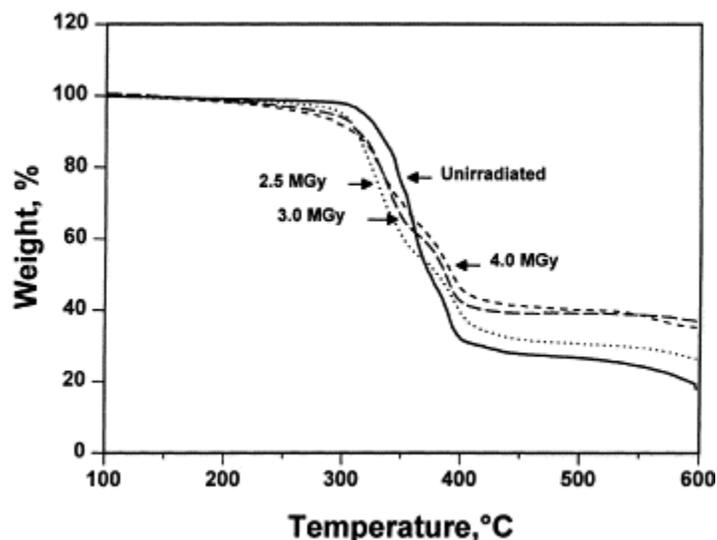


Fig. 1. Thermogravimetry of polyamide 6 containing 20 wt% (PN₂H)_n under argon. Curves of the unirradiated sample and of samples irradiated to different absorbed doses. Heating rate: 10°C/min, argon flow rate: 60 cm³/min.

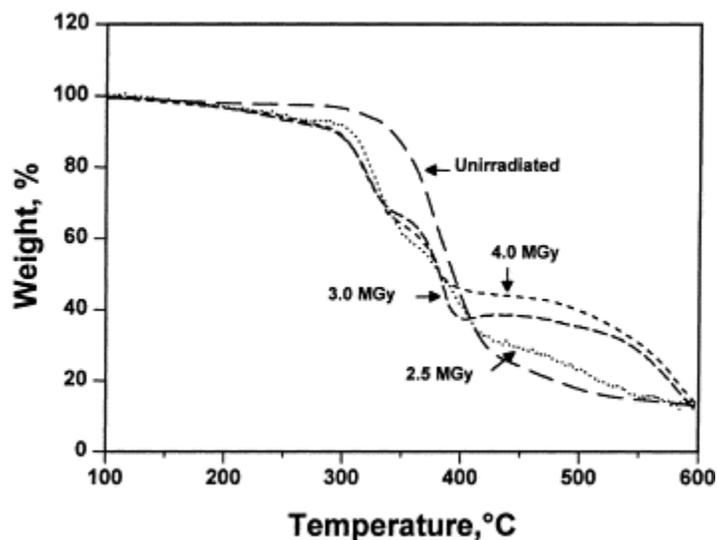


Fig. 2. Thermogravimetry of polyamide 6 containing 20 wt% (PN₂H)_n under air. Curves of the unirradiated sample and of samples irradiated to different absorbed doses. Heating rate: 10°C/min, air flow rate: 60 cm³/min.

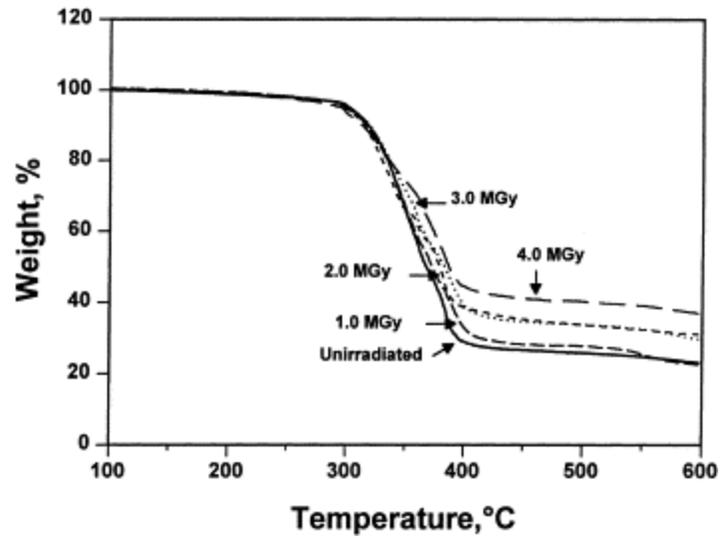


Fig. 3. Thermogravimetry of polyamide 6 containing 20 wt% (PON)_m under argon. Curves of the unirradiated sample and of samples irradiated to different absorbed doses. Heating rate: 10°C/min, argon flow rate: 60 cm³/min.

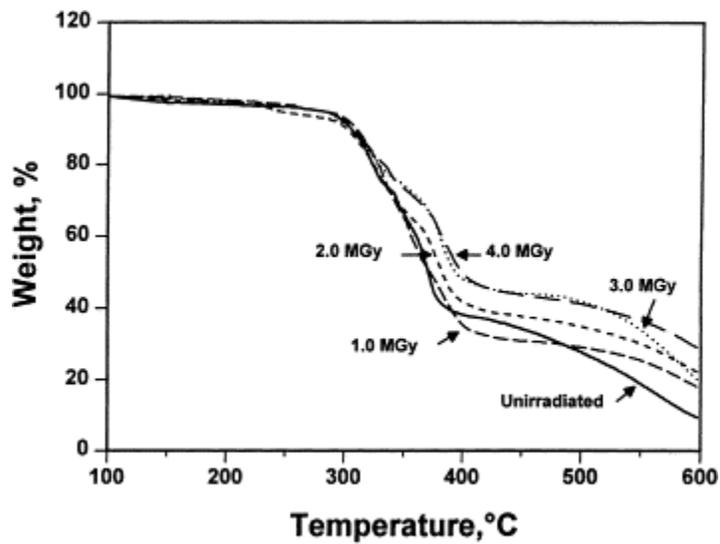


Fig. 4. Thermogravimetry of polyamide 6 containing 20 wt% (PON)_m under air. Curves of the unirradiated sample and of samples irradiated to different absorbed doses. Heating rate: 10°C/min, air flow rate: 60 cm³/min.

Table 2. Temperatures for 5% and 10% weight loss and amount of solid residue at 450°C and 600°C

Atmosphere in TGA	Absorbed dose, MGy	Temperature, °C		Solid residue, wt %	
		5% wt. loss	10% wt. loss	450°C	600°C
(PN₂H)_n					
Argon	0	317	329	28	18
	2.5	297	310	32	26
	3.0	288	312	39	37
	4.0	270	307	41	35
Air	0	314	340	24	13
	2.5	240	305	30	13
	3.0	226	291	48	12
	4.0	235	293	43	14
(PON)_m					
Argon	0	301	318	26	18
	1.0	298	315	28	23
	2.0	296	314	35	31
	3.0	299	318	36	30
	4.0	294	312	41	37
Air	0	281	304	34	9
	1.0	281	306	31	18
	2.0	244	301	37	22
	3.0	243	304	42	20
	4.0	280	306	42	29

Irradiation destabilizes the system PA-6/(PN₂H)_n as can be seen from [Fig. 1](#) and [Fig. 2](#). The 5% weight loss temperature is lowered as the absorbed dose increases. But the 10% weight loss temperature is only slightly influenced by the irradiation. The curve pertaining to the unirradiated sample of system PA-6/(PN₂H)_n shows several steps in the thermal decomposition under argon ([Fig. 1](#)) but only one step in air ([Fig. 2](#)). The degradation curves of the irradiated samples give clear indication of the occurrence of two distinct degradation processes.

In the case of the system PA-6/(PON)_m, tested both under argon ([Fig. 3](#)) and in air ([Fig. 4](#)), the onset of weight loss is not or only slightly affected by the irradiation. In fact, the temperatures of 5% weight loss (except at 2.0 and 3.0 MGy) and of 10% weight loss scatter insignificantly around constant values ([Table 2](#)). The unirradiated sample shows a two-step thermal decomposition pattern and the separation of the steps increases with increasing absorbed dose.

In the cases of both systems, PA-6/(PN₂H)_n and PA-6/(PON)_m, the solid residue fraction formed at 450°C both under argon and in air increases with increasing absorbed dose as can be seen from [Fig. 1](#), [Fig. 2](#), [Fig. 3](#), [Fig. 4](#) and [Table 2](#). The same trend holds for the solid residue fraction formed at 600°C with one exception: in the case of system PA-6/(PN₂H)_n the solid residue fraction formed in air does not depend on the absorbed dose. It seems that in the latter case the obtained residue is not resistant towards oxidation at the higher temperature which contrasts the situation met with system PA-6/(PON)_m. Here, the solid residue fraction formed in air at 600°C increases by a factor of about three when the absorbed dose grows from zero to 4 MGy. This indicates that in the case of system PA-6/(PON)_m irradiation provides significant resistance of the solid residue towards oxidation.

In this connection it is interesting to compare these results with the combustion char yields (see [Table 1](#)). This comparison shows that the combustion char yield of system PA-6/(PN₂H)_n is lower than that of system PA-6/(PON)_m and the solid residue formed in air at 600°C of system PA-6/(PN₂H)_n is also lower than that of system PA-6/(PON)_m. Therefore, in agreement with previous observations^[8] it can be concluded that char yield in the combustion of the polymer depends on the thermal oxidation resistance of the char.

4. Conclusions

⁶⁰Co-γ-rays induce crosslinking in polyamide 6 containing either phospham ((PN₂H)_n) or phosphorus oxynitride ((PON)_m). Thermal gravimetric analysis revealed that the thermal stability of the system PA-6 (PN₂H)_n decreases with increasing absorbed dose whereas it is not affected in the case of system PA-6/(PON)_m. A significant radiation-induced increase in the solid residue fraction, measured by thermogravimetry, and in the char yield determined in combustion tests, was observed with both systems, which is likely to be related to radiation-induced intermolecular crosslinking of the polyamide 6.

In the case of system PA-6/(PON)_m ⁶⁰Co-γ-ray induced crosslinking provides significant resistance of the solid residue towards oxidation which does not apply to the system PA-6/(PN₂H)_n. This gives reason to assume that the protective action of the char layer formed during combustion does not only depend on its thickness but probably also on its “quality”.

Acknowledgements

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