Obtaining of Fire-retardant Polyamide 6 Grades without Halogens for Injection Moulding

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ABSTRACT

In a great number of countries, restrictions have been imposed in using materials with high flammability and the fire retardant plastics are preferred. The fire retardant grades of polyamides represent an outstanding category in the group of this kind of polymers for injection moulding. We obtained polyamidic composites with reduced flammability by compounding polyamide 6 with melamine and concluded that introduction of 15–20 % melamine in PA 6 is an interesting possibility of obtaining fire retardant composites without halogens. Having good mechanical and flammability characteristics, these composites may be used for obtaining items for electronics and automotive industry.

Key Words: fire-retardants, polyamide, melamine, composites, injection moulding

INTRODUCTION

Uncontrolled fire is a danger to life and property. A great number of fire hazards, mostly in high populated buildings, have had, as a prime cause, the use of natural and synthetic flammable materials in their structures. This fact called the specialists' and great public's attention to the danger represented by the use of such materials.

Burning of plastics may be considered an intricate problem if the secondary phenomena involved in their burning are taken into account. A great number of plastics melt when they are heated and drips are formed. These drips help the fire spreading rapidly. In some cases emissions of toxic gases and spreading of firing pieces in atmosphere may occur [1, 2].

In these conditions a great number of regulations covering fire precautions have been imposed and the use of fire retardant plastics is strongly recommended.

Progress has been made both in developing novel and useful flame-retardants for plastics and in improving the fire test methods [3, 4].

Polyamides are successfully used in electrical, electronic and automotive applications due to their excellent mechanical properties over a wide range of

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temperatures, and their very good chemical resistance. These materials may be classified in classes V0 to V2 of UL 94 (Underwriters' Laboratory, USA). Flammability Test and their flammability may be controlled depending on the end-use domains.

For the automotive industry injection mouldable polyamide assortments with reduced flammability are of great interest [5–8].

According to the technical literature and taking into account the latest developments in this field there are some specific ways to obtain fire-retardant polyamides [5, 9–16]: –polyamides may be flame retarded by incorporating halogen-containing organic combinations together with inorganic compounds as synergists [5 9–12]; –compounding polyamides with red phosphorus or magnesium hydroxide [5, 12, 13]; –compounding polyamides with nitrogen-containing combinations such as melamine and its salts [5, 12, 14–16].

Accidentally burning or waste incineration of polyamidic composite materials flame retarded with halogen-containing organic combinations, to which antimony trioxide was added, may generate toxic (e.g., hydrochloric acid, dioxin, etc.). Due to this fact, in the last few years, the manufacturers of such materials have preferred to use flame retardant melamine and its salts [16].

Melamine is cheaper than halogen-containing flame-retardants and does not require synergetic combinations, so its use as flame retardant for polyamide 6 (PA 6) proved to be an interesting and advantageous solution from the point of view of price/performance ratio.

Moreover, flame retardation of PA 6 with melamine provides a polymer with increased processability and there are no special problems related with the chemical corrosion of the equipment.

The combustion gases of polyamide 6-melamine composites are similar to those resulting in wool or wood burning and are characterized by low toxicity [5, 14, 15].

This paper presents the results of a study concerning the preparation, properties, processability and burning behaviour of some PA 6-melamine composites.

Table 1. The characteristics of PA 6 (Relon P).

Characteristics	Value
Aspect	Cylindrical pellets with a 2 mm diameter and 2 mm length
Colour	white to light yellow
Relative viscosity in 96.5% sulphuric acid	2.7
Density at 20 °C (kg/m^3)	1130
Melting point (°C)	
–initial point, minimum	210
–final point, maximum	225

EXPERIMENTAL

In our study the following materials were used:
– Relon type polyamide 6 (Table 1) produced by S.C. Fibrex S.A. Savinesti (Romania);
– Technical grade melamine (Table 2) produced by S.C. Azo-Mures, Tg. Mures (Romania).

The studied composites were obtained using a one screw extruder (MEA-40 type, I.M. Sibiu, Romania) with a 40 mm diameter, a screw length-to-diameter ratio or L/D of 16.5 and three heating zones: solids conveying section (215–220 °C), compression and plasticating section (230–240 °C) and metering section (245–250 °C).

For assuring a better dispersion of melamine in PA 6 melt, this extruder was provided with a supplementary section (400 mm long) with Kenics static mixers, placed between the barrel and the die

Table 2. Melamine characteristics.

Characteristics	Value
Purity (%)	99.9
Volatiles at 105 °C (%)	0.1
Ash (%)	0.01
Melting temperature (°C)	354
Temperature for the beginning of sublimation (°C)	250
Combustion heat (kcal.mol^{-1})	468.9
Density (kg/m^3)	1573

Table 3. Composition (%) and codification of the realized samples for extrusion mixing of PA 6 with fire retardant agents.

Sample code	P_0	P_1	P_2	P_3	P_4
PA-6	100	90	85	80	80
Melamine	–	10	15	20	–
Decabromodiphenyloxide	–	–	–	–	15
Antimony trioxide	–	–	–	–	5

and heated at the same temperature as the die (250–255 °C).

The strands of molten polymer were then cooled in demineralized water baths and cut into pellets. The pellets, dried to 0.1 % residual moisture, were used as samples for thermal analysis. Parts of these pellets were injection moulded to obtain test specimens for evaluating mechanical and flammability characteristics.

Thermal analyses were carried out using DSC 2910 and TGA 2950 (Du Pont Instruments) modules, in a nitrogen flow, with a heating rate of 10 °C/min and 30–35 mg samples.

The injection moulding of test specimens for evaluating the mechanical properties and flammability characteristics were realized using an injection machine MITP 100/50 type (S.C. Imatex Tg. Mures, Romania) with the following characteristics: the screw diameter=35 mm, melting capacity=96 cm^3, injection pressure=120 MPa, heating zones (up to 245 °C)=4 (three on the barrel and one on the injection moulding nozzle).

Four mixtures of PA 6-fire retardant agents with the composition presented in Table 3 were realized.

RESULTS AND DISCUSSION

Thermal Behaviour

The data from thermal analyses of the composite materials were used for establishing the processing

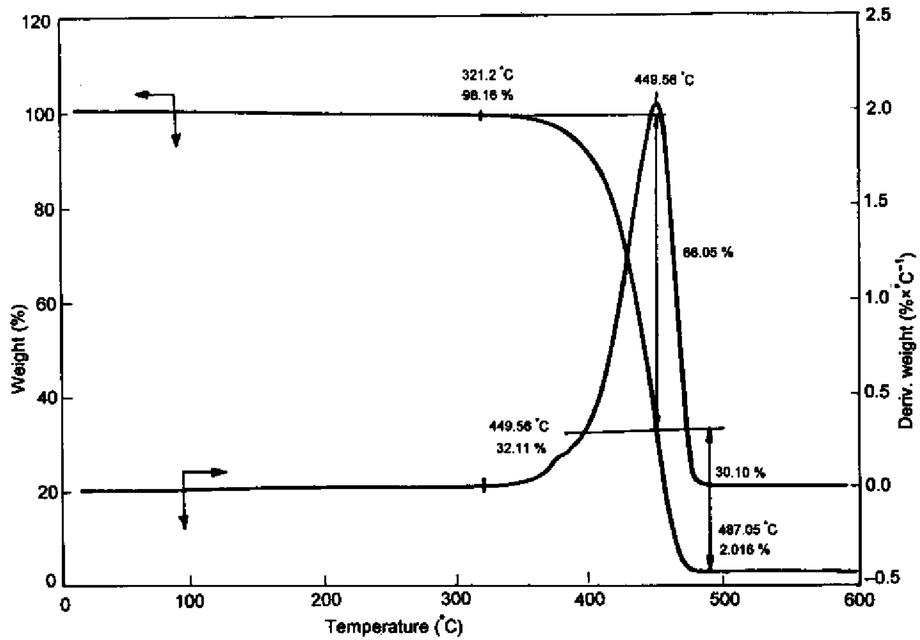

Figure 1. TG and DTG thermograms for PA 6.

conditions.

Thermogravimetric (TG) and differential thermogravimetric (DTG) curves are presented in Figures 1 and 2.

These plots highlighted the good thermal stability of PA 6 (sample P_0, Table 3), the weight loss appearing at 321.2 °C (Figure 1).

Further on heating the sample thermal decomposition was observed, with a maximum rate at 449.56 °C. Up to this temperature a weight loss of 66.05 % was noticed with a mean rate of 0.515 $\%\times°C^{-1}$. In the range 449.56–487.05 °C the mean weight loss rate was 0.803 $\%\times°C^{-1}$ and the solid residue 2.016 %.

For melamine, the TG and DTG thermograms showed the beginning of the weight loss process at 250 °C, temperature corresponding to the sublimation of this compound. The maximum decomposition rate was noticed at almost 366 °C, till 84.95% of the sample weight was lost. In the range 260–366 °C the mean decomposition rate was 0.802 $\%\times°C^{-1}$. Heating the sample between 366 °C and 387.6 °C a weight loss of 14.72 % was recorded and the solid residue was 0.36 %.

Two weight loss steps were seen in the TG curves of PA 6 with added melamine (sample P_2, Table 3). The first weight loss step, between 210–385.7 °C is likely to be due to melamine decomposition. It is interesting to notice the beginning of the weight loss before 250 °C (sublimation temperature of melamine) with a weight loss of 1.26 % at 209.74 °C; 1.73% at 240.03 °C and 2.05 % at 250.13 °C. Between 209.74 and 385.7 °C a weight loss of 18.76 % was observed, a value corresponding to the total melamine decomposition (solid residue 0.36 % at 387.6 °C, Figure 2) and to the beginning of the PA 6 thermal decomposition. For this temperature range the mean weight loss rate was 0.106 $\%\times°C^{-1}$ and the maximum one 0.245 $\%\times°C^{-1}$ at 359.74 °C.

The lower mean weight loss rate for the temperature range 209.74–385.7 °C for the composite (0.106 $\%\times°C^{-1}$) than for melamine (0.802 $\%\times°C^{-1}$

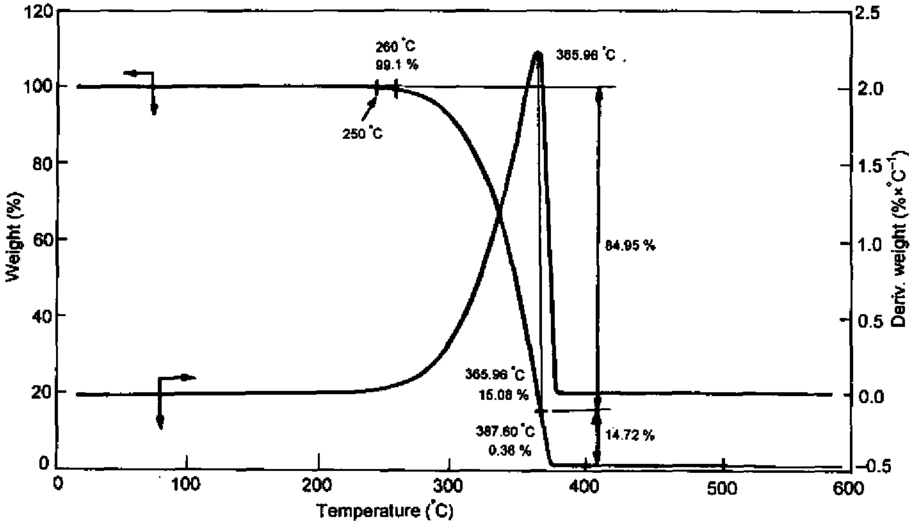

Figure 2. TG and DTG thermograms for melamine.

between 260–366 °C) suggested that PA 6 retarded the thermal decomposition of the organic compound.

The second weight loss step corresponded to the polyamide thermal decomposition. In this step a 80.12 % weight loss was observed for a temperature range 385.7– 508.3 °C. The maximum weight loss rate was 1.833 $\%\times°C^{-1}$ at 449.16 °C.

For temperatures between 385.7 and 449.16 °C the mean decomposition rate was 0.949 $\%\times°C^{-1}$ and for the temperature range 449.16–508.3 °C it was 0.336 $\%\times°C^{-1}$.

DSC curves for PA 6 (Figure 4b) and the composite material with 15 % melamine (Figure 4a) showed a slow decrease of the melting temperature (222.95 °C for P_2 as compared with 224.62 °C for PA 6).

Analyzing the traces in Figure 4, an almost identical value for the beginning of the melting range for the two samples (P_0 and P_2) was noticed while the final recorded value for the composite material (234.78 °C) was lower than for PA 6 (240.87 °C). The value of the melting heat for the composite PA 6–15 % melamine is with 14.99 $J.g^{-1}$ lower than for PA 6 (40.45 $J.g^{-1}$ as compared with 55.44 $J.g^{-1}$).

Both the melting range reduction and the decrease of the melting heat might be explained by the reduction of PA 6 crystallinity due to the dispersion of the additive in the polymer. During compounding the crystalline network of the polymer is, probably, modified.

Melamine destabilizes the PA 6 since decomposition of the formulations starts at 260 °C (for 15% melamine in PA 6, Figure 3) which is lower than onset of weight loss of pure PA 6 (350 °C). A weight loss of 1.82 % was recorded at 321.2 °C for PA 6 (Figure 1) while for the composite with 15% melamine an almost similar weight loss (2.5%) was noticed at 260 °C (Figure 3).

In the case of composites, above 260 °C, a high weight loss was recorded, and we were allowed to conclude that for injection moulding of these materials the temperature must not exceed this value.

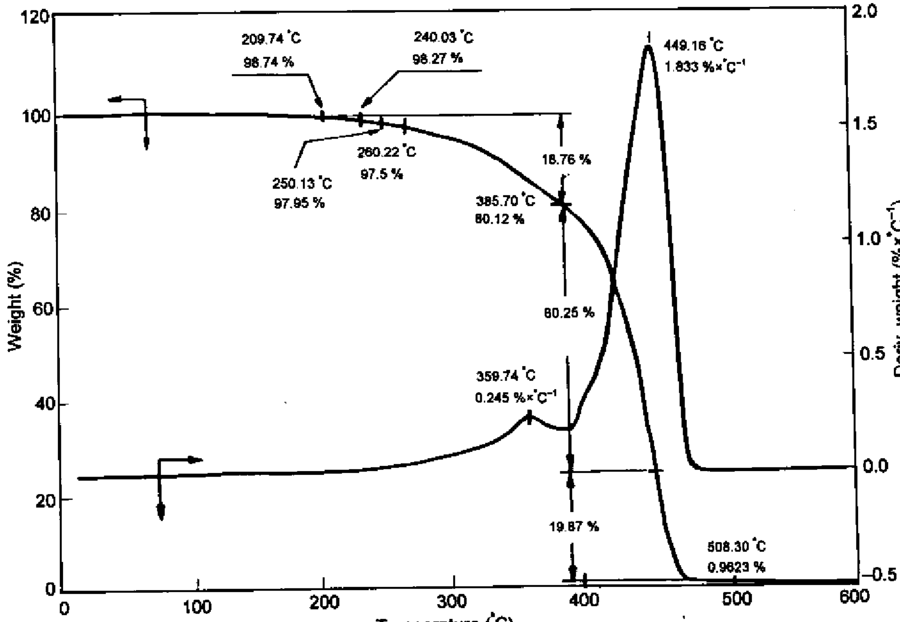

Figure 3. TG and DTG thermograms for P_2 sample (PA 6–15% melamine).

As a conclusion the maximum processing temperature for this kind of materials was established at 245 °C.

Physico-mechanical Properties

In the established processing conditions (maximum temperature 255 °C), melamine acts as a filler due to its melting point of 354 °C. As we expected, the introduction of the flame retardant was followed by an increase of the PA 6 rigidity [17].

Further evidence of this assertion was seen from the data in Table 4. The tensile strength (both at the yield point and at break), elongation at break and Charpy impact strength decreased while elastic moduli (tensile and flexural) increased with intro-duction and increasing melamine content in these mixtures.

Adding melamine up to 10 % a monotone decrease of the tensile and Charpy impact strength and a drastic reduction of the elongation at break were observed. Increasing melamine content above this value the latter characteristic remained almost un-changed.

By increasing the melamine content a continuous increase of the flexural elastic modulus was noticed while the tensile elastic modulus had a light minimum value for 10% melamine sample.

The data in Table 4 showed that although melamine had influence on the most important PA 6 physico-mechanical properties, their value still remained in a range suitable for many applications.

The physico-mechanical properties of PA 6 flame-retarded with halogens (decabromodiphenyl-oxide, antimony trioxide) are comparable with those for PA 6/melamine compositions (Table 4, sample P_4).

The Burning Behaviour

Combustion performance of the formulations was studied on 3.2 mm specimens in vertical configur-ation, based on UL 94 standard [18, 19]. The results

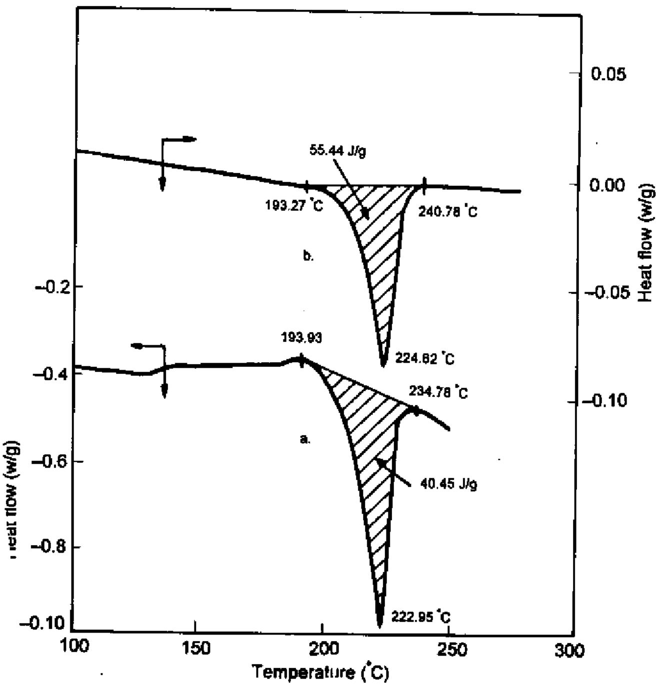

Figure 4. DSC curve for P_2 sample (a) and PA 6 (b).

Table 4. The physico-mechanical characteristics for PA 6 – melamine composites*.

Characteristics	P_0	P_1	P_2	P_3	P_4
Tensile strengths (MPa)	65.5	62.9	57.2	53.9	62
Yield stress (MPa)	75	64	57.7	54.3	63
Elongation at break (%)	100	4.5	4.4	3.7	4.8
Tensile elastic modulus (MPa)	2500	2487	2987	3362	2800
Flexural stress (MPa)	74.3	83.6	81.1	78	70
Charpy impact strength (kJ/m^2) (notched specimens)	5.5	4.8	3.8	3.6	6
Flexural elastic modulus (MPa)	2350	2550	2890	2900	2800

*Dried state proprieties, moisture < 0.2 %.

Table 5. Burning behaviour flammability test UL 94.

Sample code	P_0	P_1	P_2	P_3	P_4
Time of flame burning after each flame application (s)	max. 18	max. 4	max. 2	max. 4	max. 2
Total burning time after ten flame applications (s)	115	33	21	17	12
Flame burning or incandescence up to fastening clamp (127 mm)	No	No	No	No	No
Cotton ignition due to the falling of firing particles	A lot of falling drops, the cotton ignites	Falling drops, some igniting the cotton	Falling drops, cotton does not ignite	Falling drops, cotton does not ignite	Falling drops, cotton does not ignite

and the related observations are presented in Table 5.

Melamine provoked melt flowing and dripping of PA 6 in UL 94 test. UL 94 rating increases with increasing content of melamine. The composites PA 6-melamine have presented reduced flammability as compared with pure PA 6. Taking into account the extinguish length of times for all the composites of PA 6-melamine studied were classified in the VO class of flammability. The ignition of the cotton placed below the specimen served as a criterion of samples differentiation. This characteristic may be improved by introducing anti-dripping additives [20].

Melamine shows a little less fire retardancy as compared with halogen-containing flame retardants (Table 5), but due to its advantages, and limitations imposed all over the world regarding environmental protection, interest in melamine and its salts has increased [21].

CONCLUSION

The use of different proportions (15–20%) of melamine as flame retardant for PA 6 is of great interest in obtaining halogen-free fire retardant plastics. Using PA 6-melamine fire retardant composition most of the restrictions imposed in the case of halogen-containing additives are avoided. Materials suitable for injection moulding are obtained if the processing temperature is kept below 245 °C.

These materials with a little lower mechanical and flammability properties than in the case of using halogen-containing flame retardants have, in return, the advantage of forming non-toxic gases during burning.

Injection moulded PA 6 - melamine composites have proved useful for many specific electrotechnical and automotive applications i.e., carcasses, connectors, relay switches, fuse supports etc.

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