Polymer Degradation and Stability 97 (2012) 1215–1222

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Study on the properties of polyamide 6 blended with melamine polyphosphate and layered silicates

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ARTICLE INFO

Article history:
Received 7 November 2011
Received in revised form
14 February 2012
Accepted 6 March 2012
Available online 17 March 2012

Keywords:
Flame retardancy
Polyamides
Nanocomposites
Layered silicates
Melamine polyphosphate

ABSTRACT

In this study, the flame retardancy and physical properties of polyamide 6, melt processed in a twin-screw extruder with various amounts of melamine polyphosphate and layered silicates, were examined. Generally, there were indications that exfoliated nanocomposites were produced. During compounding, the presence of layered silicates was found to result in polymer degradation, which was further enhanced by the addition of the flame retardant. The additives were also shown to restrain the ability of polyamide 6 for crystallization. Tensile modulus and tensile strength were substantially improved, however polymer's ductility deteriorated. The incorporation of the additives exerted a positive effect also on the flame retardancy of polyamide 6, leading to materials of UL94 V-2 classification.

1. Introduction

Among the broad range of commercially available plastics, polyamide (PA6) comprises one of the most widely used due to its excellent performance/cost ratio. It is employed for a variety of applications, many of which dictate the enhancement of its flame retardancy. Quite recently, the addition of layered silicates (clay) emerged as a promising, versatile and environmentally-benign, method for improving the performance of polymers against fire. In particular, it was found that polymer layered silicate nanocomposites (PLSN) exhibit not only markedly better mechanical, thermal, and barrier properties compared to neat polymers or conventional (micro-) composites, but also, in several cases, superior fire resistance. More specifically, through cone calorimetry experiments, PLSN were proved to present a peak heat release rate significantly lower than that of the pristine matrix. The superior fire performance of nanocomposites was shown to be mainly a consequence of a protective barrier, developed on their surface during combustion, consisting of accumulated clay platelets and carbonaceous char. This superficial carbonaceous-silicate structure insulates the substrate from the external radiative heat (and the thermal feedback) and impedes the escape of the flammable volatile products of polymer degradation [1–4].

The reduction of peak heat release rate was found, however, to be the only contribution to flame retardancy of the superficial barrier, indicating that the presence of clay particles improves polymer's performance just in the regime of developing fires. When the scenario is changed to resemble a fire at the stage of ignition, the beneficial effect of the barrier formation vanishes. Therefore, PLSN fail to perform better than the clay-free analogues in the UL94 test, which is commonly performed in industry in order to examine the flammability of materials. Contrary to typical experiments in the cone calorimeter, during which the combustion of the specimen is conducted under forced flaming conditions, in the UL94 test small flames are applied resulting in the formation of a protective layer, which is not sufficiently effective to provide a significant reduction of polymer's flammability [5,6]. The failure of nanocomposites is also attributed to their dripping characteristics, which in this test play a major role: due to the presence of layered silicates, nanocomposites produce upon heating viscous melts with limited ability to favour non-flaming dripping, staying thus in place to feed the flame [7,8].

Hence, it becomes obvious that, in order to produce nanocomposites that can qualify under the UL94 protocol, clay fillers should be used in synergistic combinations with other traditional flame retardants. Due to the legislation in some countries instituted

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doi:10.1016/j.polymdegradstab.2012.03.005

for the restriction of halogenated compounds, synergists should preferably be chosen among halogen-free flame retardants [9,10]. Particularly in the case of PA6-based nanocomposites, the flame retardants should presumably act in a manner similar to that of clay fillers, given that drip-promoters, though efficient in flame retarding neat polyamides, cannot perform effectively in combination with layered silicates (they fail to decrease the melt viscosity of nanocomposites to a degree that would enable their success in the UL94 standard) [11–13]. Flame retardants that operate similarly to clay fillers during combustion are intumescent systems. On heating, these systems promote the formation of a swollen multicellular char on the surface of the polymer, capable of protecting the underlying material from the action of the flame. The development of the foamed char is the outcome of the interaction of the system's three components: the acid source (e.g. phosphate), the carbonization compound (e.g. polyol, PA6) and the blowing agent (e.g. melamine). Via the dehydrating action of the acid source, the carbonization compound produces char, which is foamed by the gases evolved by the degradation of the blowing agent [14,15].

Due to its cost effectiveness, safe handling and environmental friendliness, the intumescent flame retardant, selected to be put under investigation in this study, was melamine polyphosphate [16,17]. The main objective was to develop an environmentally-friendly, 'plug-n-play' method for enhancing the flame retardancy of PA6 along with its mechanical performance. In the pursuit of the optimum 'recipe', PA6 was melt blended in a twin-screw extruder with the clay filler and melamine polyphosphate at various quantities. The produced samples were then subjected to thorough analysis to assess the impact of the additives on important polymer properties. Hence, apart from flammability and mechanical performance, the molecular weight, the melt viscosity, the thermal transitions and the crystallinity of the prepared samples were examined.

2. Experimental

2.1. Materials

The PA6 grade (trade name: Zytel® 7301 NC010) was offered by Dupont de Nemours International S.A (Switzerland). The clay filler (trade name: Nanofil® 9) was provided by Süd-Chemie AG (now Rockwood Clay Additives GmbH, Germany); it is a natural montmorillonite, organically modified using stearylbenzyldimethylammonium chloride. The intumescent flame retardant (trade name: Ciba® Melapur® 200), a salt of melamine and polyphosphoric acid, was donated by Ciba Lampertheim GmbH (now BASF Lampertheim GmbH, Germany). Apart from the flame retardant, one more product of Ciba Lampertheim GmbH, Ciba® Irganox® B1171, was also used in this study; Ciba® Irganox® B1171 is an 1:1 antioxidant blend of a phosphite (chemical name: Tris(2,4-di-tert-butylphenyl)phosphite) and a sterically hindered phenolic-amide (chemical name: N,N′-hexane-1,6-diylbis(3-(3,5-di-tert-butyl-4-hydroxyphenylpropionamide)), and it was employed in order to restrict the potential oxidative polymer degradation taking place during processing.

2.2. Preparation of samples

The preparation of the samples involved mechanical mixing of dried PA6 (80 °C, 18 h, under vacuum) with the additives; the amount of the antioxidant blend was the same (0.25 wt.-%) in all cases, while the quantity of the organoclay and the flame retardant varied. Then, the blends were melt compounded using a twin-screw laboratory extruder (Haake Rheomex PTW16, L/D = 25). The temperature settings along the six zones of the extruder were 240-235-235-235-235-230 °C, and the screw rotation speed was 200 rpm. The resulting extrudates were named according to their composition, following the nomenclature system, as shown in Table 1.

In order to survey the influence of the extruder's operation parameters on polymer properties, selected samples were also produced by performing extrusion runs at 150 rpm using the same temperature profile as for the extrusion runs at 200 rpm.

2.3. Methods of analysis

The molecular weight (MW) of the produced samples was obtained through their intrinsic viscosity (IV), using the Tuzar and Kratchovil equation: $IV = 5.26 \times 10^{-4} MW^{0.745}$ [18]. IV was measured at 0.5 g/100 ml polymer concentration in m-cresol at 25 °C (ASTM D446), employing a Cannon-Fenske viscometer. In the case of the nanocomposites, unfiltered solutions were used and the IV was evaluated on the basis of the polymer mass, as it has been proved that the effect of clay on nanocomposites solution viscosity is quite marginal [19]. For reproducibility reasons, the IV of all samples was measured twice and the coefficient of variation (standard deviation/average) was found to be always less than 1%.

The melt viscosity, in particular the apparent shear viscosity (η), of the extrudates was obtained by transforming their melt flow rate (MFR) through an approximate conversion scheme, described elsewhere [13]. The MFR was determined in a Dynisco Kayeness Co. model 4004 capillary rheometer (Germany), according to ASTM D1238, at 235 °C. Two different ram loads, equal to 1 kg and 2.16 kg, were applied. In that way, two MFR values were recorded for each sample. In all cases, the MFR was measured at least ten times; here, the average values are presented (the coefficient of variation was less than 2%).

By performing experiments in a Siemens 5000 X-ray diffractometer (Germany), the degree of the silicates' dispersion and the crystallographic characteristics of the samples were assessed. More specifically, the patterns were recorded between 2 and 30°, with a scan rate of 2°/min, by applying an incident X-ray wavelength of 0.1542 nm (the Cu radiation source was operated at 40 kV and 30 mA). The XRD runs were carried out on films (thickness of ~1 mm), prepared by compression moulding (at 250 °C, under 200 bar) and subsequent cooling (using water of ~20 °C).

The thermal transitions and crystallinity of the produced materials were evaluated employing a Perkin Elmer Pyris 6 differential scanning calorimeter (USA). For each measurement, a sample (~10 mg) was heated at 10 °C/min, under a nitrogen atmosphere, from 30 to 250 °C, and it remained at this temperature for 3 min so that its thermal prehistory could be erased. The sample was then cooled to 30 °C and finally heated again up to 250 °C with the same rate. During cooling, the crystallization temperature (T_c), the

Table 1
Nomenclature of the prepared samples.

Abbreviation	Additives' concentration		
	Melamine polyphosphate (wt.-%)	Layered silicates (wt.-%)	Antioxidant blend (wt.-%)
0.5N/PA6	0	0.5	0.25
1N/PA6	0	1	0.25
5MP/PA6	5	0	0.25
4MP1N/PA6	4	4	0.25
5MP1N/PA6	5	1	0.25
6MP/PA6	6	0	0.25
6MP0.5N/PA6	6	0.5	0.25
6MP1N/PA6	6	1	0.25
20MP/PA6	20	0	0.25
20MP1N/PA6	20	1	0.25