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Self-extinguishing bio-based polyamides

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ABSTRACT

The fireproofing study of polyamide 11 (PA11), a bio-based polyamide synthesized from castor oil and marketed under the trade name Rilsan® is presented. As an interesting perspective, FR can be chemically linked to the PA backbone. In this way, we achieved the synthesis of a dicarboxylic acid from DOPO cycle (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide). This phosphorus diacid derivative was able to react by polycondensation to give rise of new copolyamides (coPA) bearing phosphorus moieties attached to the PA backbone with 15,000–30,000 g/mol as molar masses. The amount of phosphorus and the viscosity of the final PA were optimized. Thermal properties such as thermogravimetry analysis (TGA) or differential scanning calorimetry (DSC) were evaluated and were shown crystallinity and degradation typical of linear PA11. UL94-V0 ranking coupled with high Oxygen Limit Indexes (LOI = 40) were also obtained. Pyrolysis-combustion flow calorimeter (PCFC) and cone calorimeter were performed to understand the mode-of-action of the new phosphorus-containing FR used to obtain self-extinguishing bio-based PA11. Lastly, the preserving of mechanical properties was highlighted.

1. Introduction

Polyamides (PAs) are important engineering plastics due to excellent performances such as good processability, mechanical strength and abrasion resistance. They are widely used in electronic and transportation, textiles … However, one main limitation of these polymers is their flammability. The addition of flame retardant additives allows improving their properties and uses. Phosphorus-containing compounds [1] are well recognized for their flame retardant properties, and they are increasingly becoming more popular than the halogen ones, as they release non-toxic combustion products. Furthermore, it is recognized that the migration or leaching of flame retardants exposed to high temperature or humid atmosphere may be reduced by moving from the additive to the reactive approach [2,3]. In this latter case, flame retardant species are covalently bonded to the polymer chain that inhibits their mobility within the polymer network and maintains their efficiency over the time.

The application of reactive flame retardants (FRs) involves either the design of new polymers or modification of existing polymers. This approach combined to the use of renewable resources gives environmentally friendly flame retarded polymers. Phosphorus-containing monomers with reactive functions, such as amine or carboxyl are interesting to be used in the polycondensation of PA. Some diacids [4] obtained from the fermentation of glucose and their derivatives exist and may be used as building blocks of these new phosphorus-containing FRs (PFRs).

Derivatives based on 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) are well known as attractive alternative flame retardants for various polymers. DOPO derivatives have found applications in epoxy resins [5–10], PU foams [11], polyesters and also PA[12]. Two DOPO derivatives are commercialized under the name Safire® 3000 and XP-7866® for PA66[13] because of their high thermal stability compared to other phosphorus-containing FRs. DOPO and its derivatives are known to predominantly act by a gas-phase mechanism [11,14–16] through the formation of P-O radicals [17]. Moreover, DOPO is a H-phosphinate compound that can tautomerize to its P-OH [18] form and

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can react with nucleophilic and electrophilic species. The synthesis of reactive monomer with DOPO is easy to achieve to form DOPO diacid FR. Liu et al. [19] used DOPO grafted on maleic anhydride, which reacted with the terminal hydroxyl groups of poly(butylene terephthalate) PBT matrix. An increase of polymer viscosity and good flame-retardant properties were highlighted. Zhang et al. [20] also proposed to use DOPO-MA (maleic anhydride), as a comonomer in the synthesis of unsaturated polyester resin. Levchik & Weil [21] reported the use of reactive FR with DOPO in various polyesters and many teams [22–26] proposed different ways to obtain DOPO containing-reactive FR for flame retarded epoxy resins. Recently, Li et al. [27] grafted DOPO to SiO_2 particles to increase the thermal resistance of PA6 composites and permit the time-stability of DOPO in the polymer, but it is not clearly a reactive FR for PA. To the best of our knowledge, DOPO diacid derivatives have been reported for the first time in patent literature [28] in 1977, then in 1998 by a german team [29], and more recently some chinese patents [30–33] claimed the use of DOPO diacid derivatives to give flame retardancy properties to PA6 or PA66 by copolycondensation. This FR reacted with a diamine monomer to form a prepolymer with a terminal amino group then the FR prepolymer was added in a polymeric medium in the presence of a catalyst at high temperature for 6–14 h. No information on the molar masses and no comprehension on flame retardancy mechanism were done.

In this present study, 3-[10-(9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide-10-yl)]itaconic acid (DOPO-ITA) was synthesized and successfully used to prepare novel PA11/10-10/10-DOPOITA copolyamides with phosphorus-containing pendant groups. The mechanical, thermal and flame retardancy properties were studied and compared to those of Rilsan® [34] were investigated.

2. Experimental part

2.1. Reagents and materials

9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) was purchased from ABCR. Itaconic acid was obtained from Sigma-Aldrich. 11-aminoundecanoic acid (AC11), decane-1,10-diamine (DA10), decan-1,10-oic acid (DC10) and commercial available polyamide 11 commercial grade as reference were provided from Arkema. All the reagents were used without further purification.

Chemical structures of the prepared compounds were determined by ^{31}P NMR and ^{1}H NMR spectroscopies in a Bruker Avance 400 MHz spectrometer at room temperature in $(CD_3)_2CO$ solutions. External references were trimethylsilane (TMS) for ^{1}H NMR and phosphoric acid (H_3PO_4) for ^{31}P NMR. Shifts are given in ppm. The molar masses of the polyamides were determined by gel permeation chromatography GPC (Waters Alliance 2695 and 2 columns PSS PG 100A and 1000A) that was calibrated with polymethylmethacrylate (PMMA) standard in hexafluoroisopropanol solvent at 40 °C. The potentiometric titration was made on samples in solution with a combined electrode. The viscosity analyses were achieved in meta-cresol solution. To measure the phosphorus ratio after polymerization, a portable X-Ray Fluorescence analyzer XMET 5100 was used. Analysis time was 60 s. The phosphorus content was assessed from the Kα radiation and a phosphonated epoxy resin called IL with a known phosphorus content equal to 1.75 wt% was used as reference.

Differential Scanning Calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, n-octadecane and n-octane standards. Nitrogen was used as the purge gas. The thermal properties were analyzed at 20 °C/min between −20 and 240 °C to observe the glass transition temperature determined as the inflexion value in the heat capacity jump and the residual curing, the melting and crystallization temperatures, endothermic and exothermic peaks, respectively. Thermogravimetric analyses (TGA) were carried out to determine the weight-loss temperature by heating from room temperature to 750 °C at a rate of 10 °C/min under nitrogen using a TGA Setsys Evolution from Setaram. Flammability was assessed using a Pyrolysis-combustion flow calorimeter from Fire Testing Technology (FTT UK). About 3 mg was placed in the pyrolyzer, undergoing an increase of temperature from 20 °C to 750 °C at 1 °C/s under a nitrogen flow. Pyrolytic gases were sent to a combustor heated at 900 °C under air flow ($N_2/O_2 = 80/20$). At this temperature and with 20% of oxygen, combustion was considered to be complete. Heat release rate was determined by oxygen depletion according to Huggett principle [35] (1 kg of consumed oxygen corresponds to 13.1 MJ of heat released). PCFC analyses correspond to anaerobic pyrolysis followed by high temperature oxidation of decomposition products (complete combustion [36]). Peak of Heat Release Rate (pHRR) is the maximal value of the heat release rate. TpHRR is the temperature at pHRR. The total heat released (THR) was obtained by integration of PCFC curves. All samples were tested in triplicate. The uncertainties are typically 5 °C, 50–100 W/g and 1 kJ/g for TpHRR, pHRR and THR, respectively. Fire behavior was also studied using a cone calorimeter (Fire Testing Technology) which is a powerful tool to investigate the fire behavior of polymers. A horizontal sample sheet of $100 \times 100 \times 3$ mm^3 was placed at 2.5 cm below a conic heater and isolated by rock wool. The samples were exposed to a 35 kW/m^2 heat flux in well-ventilated conditions (air rate 24 L/s) in the presence of a spark igniter to force the ignition. HRR was determined according to oxygen depletion (Huggett's relation) as in PCFC. This test was performed according to the ISO 5660 standard. PA11 commercial grade reference and PAx/0.5P were tested in duplicate. The limited oxygen index (LOI) and UL94 ranking were measured according to ASTM D2863 standard and according to the ISO 9772 standard on sample bars. 3 mm thickness sample bars ($127 \times 12.7 \times 3$ mm^3) were made in a standard steel mold. Dynamic Mechanical Analyses (DMA) were carried out on DMA Q800 TA instruments. Uniaxial stretching of samples was performed while heating at a rate of 2 °C.min^{-1} from −50 °C to melting point of samples, keeping frequency at 1 Hz and amplitude at 15 μm.

2.2. Synthesis of flame-retardant polyamides and melt processing

2.2.1. Synthesis of DOPO-ITA

The DOPO-ITA comonomer was synthesized according to the method used by Chang and Chang [37]. In a two-necked glass flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser, 15.03 g (0.115 mol, 1 eq) of itaconic acid and 24.97 g (0.115 mol, 1 eq) of DOPO were added. The mixture was stirred at 155 °C for 6 h. At the end, it was frozen and ground to obtain a white powder of DOPO-ITA with a 97% yield. The phosphorus ratio was 9 w% in this flame retardant product.

^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ: 2.45 (2H, H_1); 2.69 (2H, H_3); 2.98 (1H, H_2); 12.44 (2H, H_4); 7.29–8.20 (8H, $H_{aromatic}$).

^{31}P NMR (162 MHz, DMSO-d_6, ppm): δ: 35.32 and 35.75.

2.2.2. Synthesis of copolyamides by polycondensation

Reactions were carried out in a glass tube with a head equipped of mechanical stirrer and a nitrogen inlet. The reagents were added in ascending melting point and they were heated at high temperature. The temperature and the viscosity (at the molten state) of the system were continuously monitored and controlled. The polycondensation was stopped when the viscosity remained constant. The studied compositions are summarized in Table 1.