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Carbamate end-capped poly(oxymethylene) copolymer with enhanced thermal stability prepared by reactive extrusion

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ABSTRACT

Carbamate end-capped poly(oxymethylene) (POM) copolymer was prepared by reactive extrusion and its stability has been studied by means of thermogravimetric analysis (TGA) both in air and in nitrogen, content of formaldehyde generated (C.F.G) and isothermal weight loss. 4, 4′-diphenylmethane diisocyanate (MDI) was used as an end-cap agent to react with POM molecules during extrusion. MFI results and FTIR spectra indicate that MDI did react with POM, which replaced the labile hydroxyl chain ends with thermally more stable carbamate structures and at the same time increased the molecular weight due to chain extension or possible branching. At low MDI contents (≤1 wt%), end-capping dominated the procedure while chain extension or possible branching occurred more frequently with the increase of MDI, resulting in the continuous reduction of MFI. The presence of branched or crosslinked structure has been verified by the huge difference between weight-average molecular weights deduced from two different methods and melt flow ratio. Side reactions also occurred during extrusion, including the self-polymerization of MDI and reactions between MDI and active-hydrogen containing compounds. According to TGA and C.F.G results, crude M90 extruded with MDI showed superior thermal stability to either original crude M90 or commercial POMs. Similar stabilization effect can be found in commercial M90 and commercial M270 but was less prominent because of their inherently better stability. Such stabilization effect depends largely on end-capping, although some of it should attribute to the roles of formaldehyde absorbent the carbamate structures and side products played. Thermal stability of crude M90 with 1 wt% MDI was further improved through the addition of stabilizer package. After end-capping, the mechanical properties of the POM still remained at an acceptable level.

1. Introduction

Poly(oxymethylene) (POM), also known as polyacetal, is an important engineering plastic with high crystallinity. Due to its excellent properties including high strength, stiffness and chemical resistance, this engineering plastic gets itself an extremely wide application in various fields. While POM is inherently unstable with the existence of hemiformal chain ends, it undergoes depolymerization easily accompanied by the evolution of formaldehyde, which accelerates the degradation in return by acidolysis when oxidized into formic acid [1–4]. Therefore, seeking for ways of stabilization is crucial to POM researchers.

DuPont developed a method to end-cap POM with acetic acid or acetic anhydride through condensation to replace the labile hemiformal groups with stable terminals [5], but once the degradation is initiated, it leads to a complete unzipping of the whole molecular chain. Whereas Celanese used a method of copolymerizing trioxane with a second monomer like ethylene oxide or 1, 3-dioxolane [6] which also achieved a good stability because of the distribution of –CH2–CH2– segments in polymer main chains. These segments can decelerate or even stop the depolymerization because further degradation requires a new initiation [7]. Nevertheless, this kind of POM copolymer is still unstable because of the presence of labile chain ends, which need to be further eliminated or replaced. Thus, some ways of terminal stabilization have been introduced.

Terminal stabilization can be achieved by the selective decomposition of unstable terminals in the temperature range of 120 °C–230 °C [8]. One known method is to heat the polymer in water or organic solvent with the presence of base which is capable

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of hydrolyzing the unstable terminals [9,10]. Another simpler method is continuous melt processing [11,12], which is usually conducted with a screw extruder in the temperature range of 190 °C–240 °C. However, despite the incomplete elimination of unstable terminals, this method could also lead to the scission of polymer main chains which generates new labile chain ends and reduces the molecular weight.

Herein, we present a new method involving an end-capping agent and the process of extrusion to achieve the terminal stabilization of poly(oxymethylene) copolymer. We've chosen isocyanate as the end-capper, thus, 4, 4′-diphenylmethane diisocyanate (MDI), to be specific, for the fact that single functional isocyanates usually evaporate during extrusion because of their low boiling temperatures. This paper aims to eliminate the labile hemiformal chain ends of POM through reactive extrusion, with MDI as the end-capping agent to form a thermally more stable structure of carbamate. The thermal stability of this carbamate end-capped poly(oxymethylene) copolymer has been studied.

2. Experimental

2.1. Materials

The POM copolymers including crude M90 (MFI = 9.0 g/min) powder without any additives, commercial heat-stabilized M90 (MFI = 9.0 g/min) and M270 (MFI = 27.0 g/min) pellets were supplied by Yunnan Yuntianhua Co., Ltd., 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol (HFIP) was supplied by DuPont. MDI, ethanol, Irganox1010, PA6 and $Mg(OH)_2$ used in this study were also commercial available products. POM copolymers of Duracon (Polyplastics) and N2320 (BASF) were used for comparison.

2.2. Preparation and purification

The carbamate end-capped POM was prepared by reactive extrusion. Crude M90, commercial M90 and commercial M270 with different contents of MDI were mixed and extruded by a SHJ-20 twin-screw extruder (Nanjing Guangda Chemical Equipment Co., Ltd.) at the rotational speed of 120 rpm with the barrel temperature in the range of 200 °C–210 °C, and then pelleted. All POM samples were oven-dried at 80 °C for 4 h both before and after extrusion.

Extrudates of crude M90 with MDI content of 1 wt% and 5 wt% were purified to remove any side products for further study. The purification procedure followed the method given by Hasegawa et al. [13]: POM pellets were fully dissolved in HFIP at room temperature, the resulting HFIP solution was poured into ethanol to precipitate POM. Then the POM thus precipitated was filtered and oven-dried at 80 °C for 4 h.

2.3. FTIR analysis

POM thin films for FTIR test were prepared in an oven at 190 °C by clipping two pieces of slide glass together with samples squeezed in the gap. The measurement was conducted on a Nicolet Magna 560 IR spectrometer (SpectraLab Scientific Inc.) at a resolution of 4 cm^{-1}, from 400 cm^{-1} to 4000 cm^{-1}.

2.4. Melt flow index (MFI)

The melt flow index was measured by a CS-127 melt flow index tester (Custom Scientific Instruments, Inc.) with an applied mass of 2.16 kg and cylinder temperature of 190 °C according to ISO 1133. MFI with an applied mass of 10.0 kgg at 190 °C was also measured to obtain melt flow ratio (MFI measured under 10.0 kg/MFI measured under 2.16 kg). The molecular weight (M_w) of POM was calculated by the formula below:

$$\mathrm{MFI} = 1.30{*}10^{18} M_w^{-3.55}$$

where the MFI is the melt flow index measured with an applied mass of 2.16 kg at 190 °C.

2.5. Intrinsic viscosity measurement

The intrinsic viscosity of different POM samples was measured according to HG/T 3604-1999. 98 wt% 4-chlorophenol and 2 wt% α-pinene were mixed as solvent, 0.1 g chopped POM sample was dissolved in 100 mL of the mixed solvent (0.1 g/dL). The time it took for both solvent and solution to pass through two calibrated marks on the Ubbelohde viscometer with a proper diameter was recorded in order to calculate η. Then the weight-average molecular weight (M_w) can be derived from the formula below:

$$[\eta] = 4.13{*}10^{-4} M_w^{0.724}$$

where η is the intrinsic viscosity of POM samples.

2.6. Rheological characterization

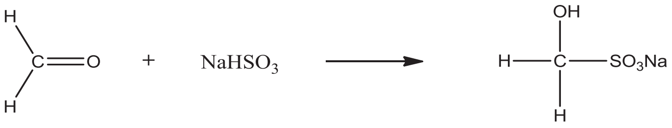
The rheological characterization of POM samples were determined at 200 °C in nitrogen atmosphere by AR2000ex-type rotational rheometer with two parallel plates with a diameter of 25 mm and a gap width of 1.0 cm. The scanning frequency was from 0.005 to 100 Hz. The diameter of the samples was 25 mm, and the thickness was 1.0 cm.

2.7. Thermogravimetric analysis

Thermogravimetric investigations of POM samples were carried out with a TA Instruments SDT-Q600. Samples of 8–10 mg were heated under nitrogen and air atmosphere with a gas stream of 100 mL/min at a heating rate of 10 K/min.

2.8. Concentration of formaldehyde generated (C.F.G)

The C.F.G was measured by the following procedure: oven-dried POM samples were heated in a conical flask at 220 °C for 60 min, the formaldehyde generated during heating was blown into distilled water by nitrogen stream (flow rate: 200 mL/min). The estimation of formaldehyde was determined by bisulfite method [14] – excessive solution of 0.2 wt% sodium bisulfite was poured into the distilled water containing formaldehyde, the reaction can be described by the equation below:



Then titrate the unreacted sodium bisulfite with standard iodine solution:

$$NaHSO_3 + I_2 + H_2O \rightarrow 2HI + NaHSO_4$$

0.2 wt% sodium bisulfite solution of same volume was prepared for blank test. The C.F.G was calculated by the following formula: