Molecular Design of Reactive Flame Retardant for Preparing Biobased Flame Retardant Polyamide 56

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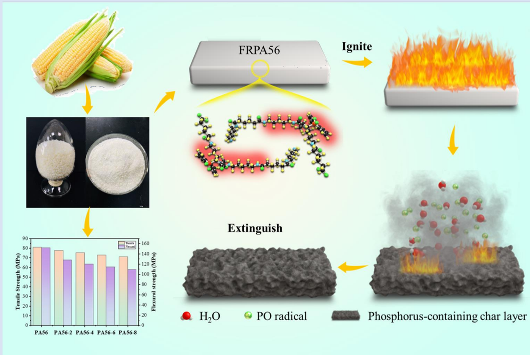
Abstract

Polyamides (PA) are widely used for their excellent mechanical properties, thermal stability, chemical resistance and good processability, gradually replacing traditional metal and ceramic materials in several emerging fields. As resource and environmental issues become increasingly prominent worldwide, bio-based polyamides show attractiveness due to their renewable and low carbon emission characteristics. PA56, whose monomer glutamine is derived from starch, is a semi-bio-based polyamide with comprehensive performance similar to PA66 and has broad application prospects.

However, PA56 has the disadvantages of flammability and melt drip. Traditional blending modification is difficult to solve the major problems of compatibility and dispersion, resulting in a significant reduction in overall performance. In this paper, a high temperature resistant, water-soluble copolymer flame retardant is synthesized and copolymerized with PA56 to prepare FRPA56, which exhibits good flame retardant properties, excellent heat resistance, mechanical strength.



Results and discussion

1. Synthesis of flame retardants and FRPA56

As shown in **Figure 1**, the copolymeric flame retardant DOPDA was synthesized from bio-based itaconic acid, 1,5-pentanediamine and DOPO, and its good temperature resistance and water solubility ensured the homogeneous copolymerization with PA56. Subsequently, FRPA56 resins with different flame retardant contents were produced by one-step melt polycondensation.

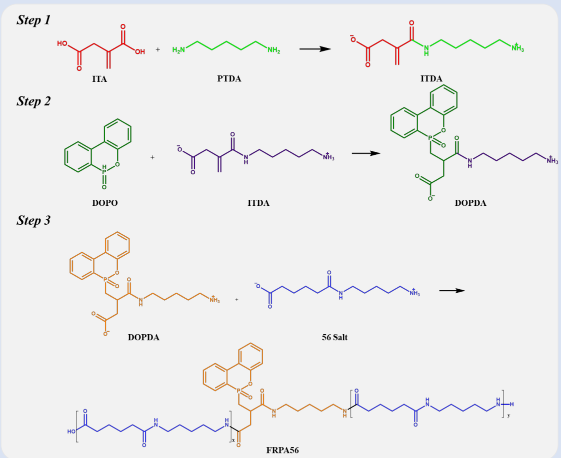


Figure 1. Preparation of copolymeric flame retardants and FRPA56.

2. Structural and thermodynamic properties

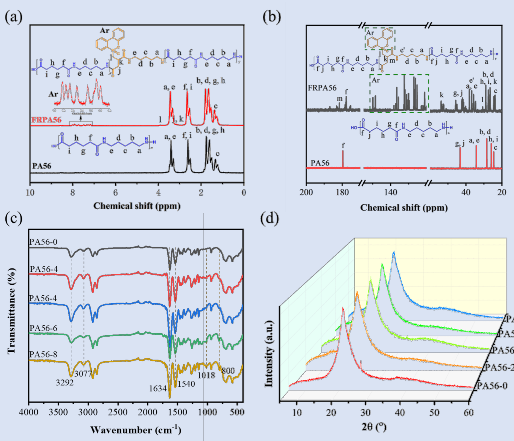


Figure 2. ^{1}H-NMR (a), ^{13}C-NMR (b), FTIR spectrum (c) and XRD pattern (d) of FRPA56.

Table 1. Thermomechanical properties of FRPA56.

Samples	T_m (°C)	T_g (°C)	T_c (°C)	$T_{5\%}$ (°C)	T_{max} (°C)	ΔH_m (J/g)	Crystallinity (%)
PA56	256.6	58.3	195.4	371	396	55.29	29.3
PA56-2	254.0	60.7	185.0	363	390	52.08	27.6
PA56-4	251.8	63.1	177.8	354	382	47.30	25.1
PA56-6	248.7	66.3	175.3	344	376	43.49	23.0
PA56-8	246.1	69.4	173.1	330	371	40.19	21.3

3. Mechanical and physical properties

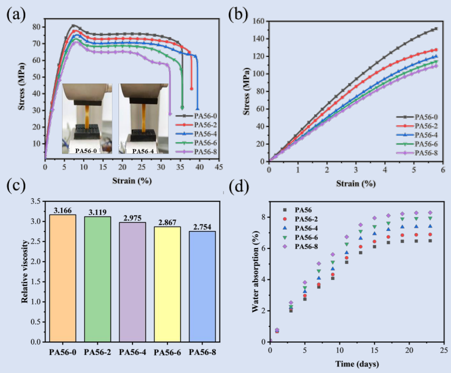


Figure 3. Stress-strain curve (a), Flexural property (b), Relative viscosity (c) and Water absorption (d) of FRPA56 with different flame retardant content.

As shown in **Figure 3**, the copolymeric flame retardant modification caused a slight decrease in tensile strength and flexural modulus of PA56, and the elongation at break showed a trend of increasing first and then increasing. Moreover, as the flame retardant content increased, the relative viscosity decreased slightly due to the larger flame retardant site resistance, while the decrease in crystallinity caused an increase in water absorption.

4. Flame retardant properties

As shown in **Table 2**, the LOI of PA56 was 24.6%, and increased with the incorporation of flame retardant. When the addition content was 6wt%, the LOI of the sample strip was over 28%, which had good flame retardant performance. Figure 4 shows the vertical burning test results of FRPA56. When the flame retardant content was lower than 4*wt*%, the flame retardant grade is V-2. While the flame retardant content was 6*wt*%, the sample strip will extinguish quickly and reached V-0 grade with excellent flame retardant performance.

Table 2. Limiting oxygen index of FRPA56

Samples	PA56	FRPA56-2	FRPA56-4	FRPA56-6	FRPA56-8
LOI %	24.6	25.3	26.9	28.4	29.7

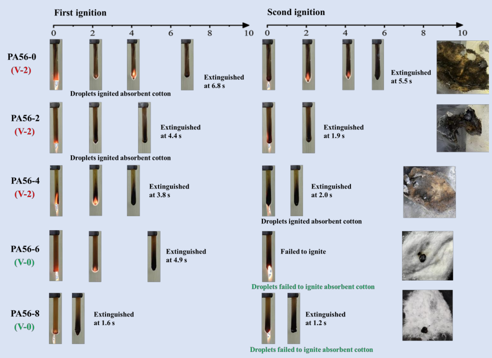


Figure 4. UL-94 vertical burning test results of FRPA56