

Synthesis and Mechanical Property Study of a Aromatic Copolyamide

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Polyamide is notable for its extreme durability and strength. We designed and synthesized a series of copolymers using metaphenylene diamine, isophthalyl chloride and terephthalyl chloride. Intrinsic viscosity and impact strength were tested respectively.

During the synthesis, interfacial polymerization and solution polymerization were utilized. Interfacial polymerization has fast reaction rate but it's hard to control. Meanwhile the surfactant and salt may be mingled with polymers and affect mechanical properties. On the other, solution polymerization is more suitable for scale up production but may lead to solvent recovery problem. As shown in the graph below, solution polymerization have relatively high intrinsic viscosity (about 180-220 ml/g) and specific viscosity (about 1.0-1.5), whereas interfacial polymerization only gives intrinsic viscosity between 130-180ml/g and specific viscosity between 0.8-1.3. In interfacial polymerization, when polymer chain grows to a relatively high length, it will precipitate from the reaction system. In addition, water as solvent will hydrolyze acyl chloride and lead to unequal reaction mole ratio. This relatively low molecular weight leads to low polymer viscosity.

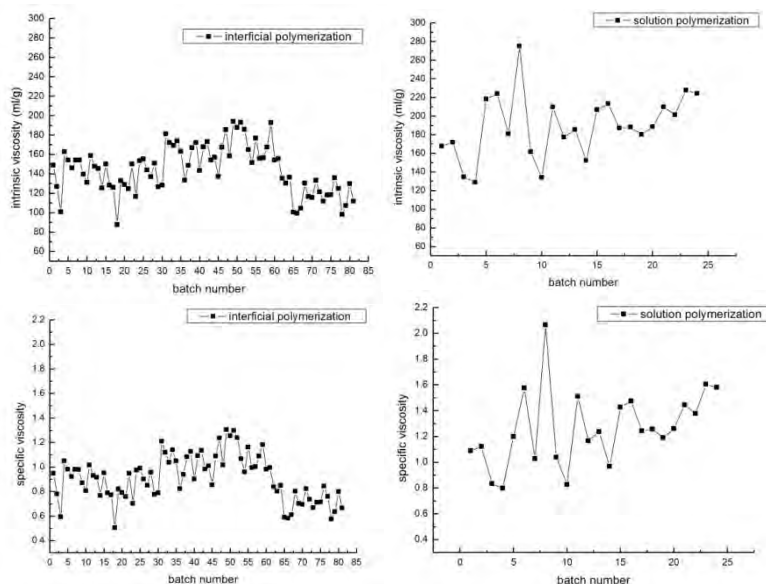


Fig 1. intrinsic and specific viscosity by interfacial and solution polymerization

In solution polymerization, different reactant ratio can control molecular chain length, which will affect polymer viscosity and impact strength. When the reaction ratio between amide and acyl chloride reaches 1:0.990, material already has a high intrinsic viscosity. But impact strength reaches a high

value only when the reaction ratio is near 1:1. Results are shown in table 1.

Table 1. relation between reaction ration and impact properties

Amide: acyl chloride (molar ratio)	Intrinsic viscosity (ml/g)	Specific viscosity	Impact strength (kJ/m ²)
1:0.985	89.585	0.518	Unable to molding
1:0.990	128.729	0.792	13.5
1:0.995	175.395	1.152	12.6
1:1	201.58	1.378	91.6

The change of intrinsic viscosity and impact strength during reaction time is also studied. In the initial 0.5h after feeding, there generated some high molecular weight chain because of reaction inhomogeneity. This high molecular weight part led to a high intrinsic viscosity and impact strength of the material. As time went on, reaction approaches homogeneous. Segment exchange reduced Mw, which is closely related to IV and impact factor. After 2.5-3 hours, the reaction approach equilibrium (Fig 2).

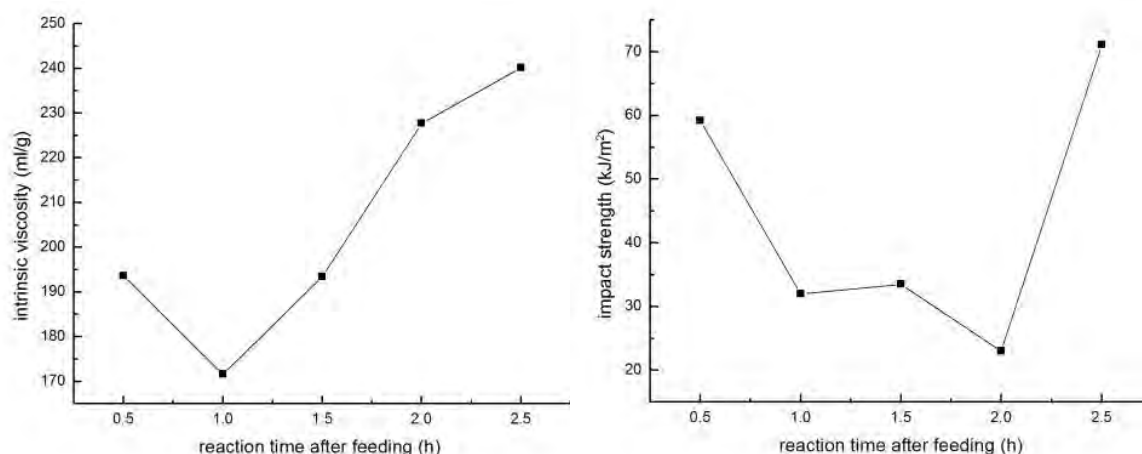


Fig 2. Intrinsic viscosity and impact strength change with reaction time

Sequential structure also has effects on impact strength. Polymers with terephthalyl chloride forming continuous chain segment have high impact strength and low impact strength (table 2. Batch no. 13422, 13709, 12Y06, 12Z29). On contrary, when isophthalyl chloride and terephthalyl chloride form radom structure (batch No.14609, 14610), material will have high impact strength but low intrinsic viscosity. This is more beneficial to material processing and suitable for die-casting molding which can easily induce chain orientation.

Batch No	Intrinsic viscosity (ml/g)	Specific viscosity	Impact strength (kJ/m ²) (compression molding)	Injection Molding (Y/N)
13422	161.77	1.040	97.2	N
13709	213.30	1.476	80	N
13Y06	209.81	1.445	61.4	N
12Z29	201.58	1.378	91.6	N
14609	177.16	1.172	>100.0	Y
14610	182.00	1.214	>100.0	Y

Conclusion:

Compared with interfacial polymerization, solution polymerization can obtain polymers with higher intrinsic viscosity. Aromatic nylon shows high intrinsic viscosity even in a relatively low molecule weight, but impact strength goes up only when reaction ratio is near 1:1. As reaction time goes on, intrinsic viscosity and impact strength first decrease then increase and reach equilibrium at 2.5-3h after feeding. Sequential structure can affect polymer processing to a large extent. Polymers with isophthalyl chloride and terephthalyl chloride forming random structure will decrease segment orientation and have better impact properties.