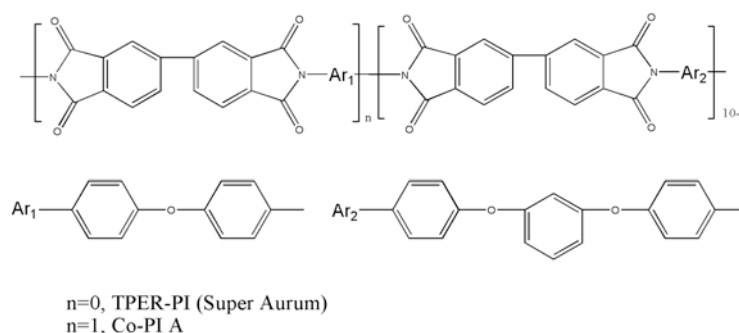


Melt processable and High performance Semi-crystalline Polyimide

Wei Wang, Xiaogang Zhao, He Jia, Guodong Dang, Daming Wang, Chunhai Chen*
 Alan G. MacDiarmid Institute, Jilin University, Changchun 130012, China
 E-mail: cch@jlu.edu.cn; Tele: +86-85168335

Since semi-crystalline polyimides offer advantages of increased solvent resistance and retention of mechanical properties above the glass transition temperature. These features have made semi-crystalline polyimides the focus of considerable research over the recent years. As one of typical semi-crystalline polyimides, Super Aurum® could be melt processing easily, and can be crystallized rapidly, fully reflect the advantages of crystalline polyimide and can be used at 359 °C for long time. However, due to the high melting temperature, the required processing temperature must be higher than 400 °C, which is near the upper bound of thermal stability. In addition, due to the high crystallization rate, it is very difficult to quench Super Aurum to amorphous, so during practical processing, most products are highly crystallized and too brittle, types and applications of products are highly limited.

The work reported here is to prepare a new high performance engineering plastics, which will also be thermal stabile, semi-crystalline, inexpensive and melt processable. 4, 4'-ODA was used to copolymerize with Super Aurum®, a new semi-crystalline polyimide material was expected.



A series of semi-crystalline molding powders were synthesized according to the diamine composition, phthalic anhydride (PA) was used as end capper to control molecular weight and maximize the thermal stability. It is well known that the properties of crystalline polymer are strongly dependent on the crystalline structure formed during processing. In order to search for the optimum processing conditions in an industrial process and to obtain products with better properties, it is significant to study the isothermal and non-isothermal crystallization

process quantitatively. First, Jeziorny analysis, Ozawa analysis and an approach proposed by MO Zhishen were applied to study the non-isothermal crystallization behaviour of TPER PI. The results suggested that TPER PI has fast crystallization kinetic, the apparent Avrami exponent n obtained by the Jeziorny method was 2.4 and then changed to 3.5 when cooling rate reached 20 K/min, indicating the mechanism of nucleation or the way of growth have changed. Then, Avrami equation was used to analyze isothermal melt crystallization progress of TPER PI and Co-PI A. Avrami exponent n for TPER PI was found to be 2.1 at 345 °C and increased to 3.6 at 360 °C. Avrami exponent n for co-PI was found to be 1.8 at 295 °C, which increased to 2.7 at 335 °C. The results indicated that primary crystallization processes had changed as the introduction of 4, 4'-ODA. Activation energy ΔE for TPER PI and co-PI were found to be -404 kJ mol⁻¹ and -86 kJ mol⁻¹ by Arrhenius form, indicating higher activity of TPER PI. Since practical processes such as extrusion, molding and film production usually are performed under dynamic, non-isothermal crystallization conditions, so it is very important to study the non-isothermal crystallization kinetic of polymers. Jeziorny analysis, Ozawa analysis and Mo's approach were used to investigate non-isothermal cold crystallization progress. Three-regime behavior and two-regime behavior were found in TPER PI and co-PI by Jeziorny analysis, which indicated the secondary crystallization reduced in co-PI under non-isothermal condition. Ozawa analysis was found to be not applicable to analyze non-isothermal crystallization kinetics of TPER PI and co-PI. A series of straight lines obtained from Mo's approach, α was 1.0 and 1.3 for TPER PI and co-PI, respectively. Activation energy ΔE_{non} for TPER PI and co-PI were found to be 247 KJ mol⁻¹ and 193 KJ mol⁻¹ by Kissinger Equation. The kinetics parameter $F(T)$ by Mo's approach and ΔE_{non} indicated that co-PI exhibited higher crystallization rate than TPER PI during cold crystallization progress.

Starting from melt processing point of view, rheological studies have been carried out. Effect of imidization temperatures, molecular weights, monomer compositions, melt temperatures, melt time on melt viscosity had been investigated, respectively. Results indicated that the co-PI A exhibited much lower melt viscosity compared to TPER PI.