

## Chapter 2

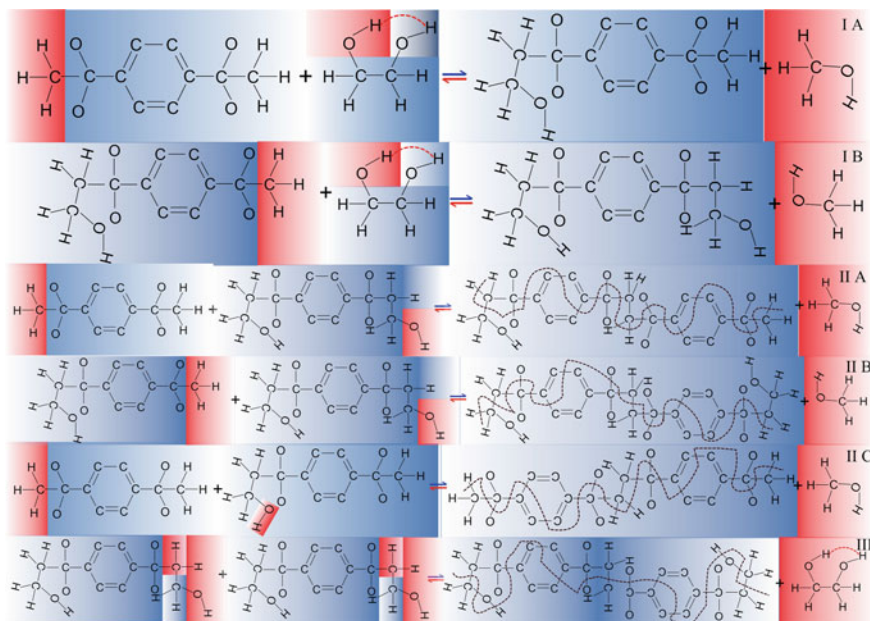
# Manufacturing Process of Thermally Unstable Partially Oriented Yarns

**Abstract** The metamorphosis of tuPOY from basic organic raw materials to an advanced conducting fiber having metallic properties is discussed in this chapter. A step by step process of embedding conduction and radiation properties in tuPOY, with an elaborated stagewise analysis is presented. The production process is justified with parametric evaluation and analysis. Production process flow from a commercial manufacturing viewpoint is outlined.

**Keywords** Thermal instability · Polymerization · Transesterification · Polycondensation · Retardant · Energy barrier

A specific property of polyester based yarn is its thermal instability at a particular stage during the production process [1–7]. The existent polymerization of POY seeks to remove the molecular instability through a polycondensation process. In the proposed work, this instability is taken advantage of and the reaction is arrested in the polycondensation stage to obtain an unstable tuPOY. The reaction mechanism initiates with the esterification of purified Dimethyl Terephthalate (DMT) and Ethylene Glycol (EG) in a ratio of 1:3, which produces oligomer, as shown in the reactions 1–3 (Fig. 2.1).

Reaction I, includes a complex of EG with carbomethoxy groups of DMT, methyl  $\beta$ -hydroxyethyl terephthalate and with oligomers containing carbomethoxy end groups. The reaction produces bis-hydroxyl ethyl terephthalate (BHET) as the main monomer. Reaction II entails a complex of transesterification reactions of carbomethoxy group with the carbo-hydroxyethoxy groups of bis- $\beta$ -hydroxyethyl terephthalate ( $\beta$ -BHET) and all oligomers containing carbohydroxyethoxy groups. Reaction III outlines the two stage condensation reactions of the carbohydroxyethoxy group. During polycondensation process the oligomers and polymer chains combine to produce lengthened chains in efforts to stabilize their entropy. The thermally unstable reaction is arrested at this point using an innovatively proprietary retardant. The retardant forms an alternating barrier between the  $C-H$ ,  $C-C$  and  $C-O$  chains preventing the breaking or forming of any further chains of oligomers. An advantage of the innovative retardant is that, it does not react with the oligomers and the end product shows no reactivity with the formulated retardant. Furthermore, the reaction is arrested in the third stage because at this stage all the properties of the textile



**Fig. 2.1** Reaction mechanism occurring during the production of tuPOY. (1) Shows the complex esterification mechanism forming oligomers, (2a–c) shows the complex transesterification of the oligomers within themselves to form polymer chain, (3) shows the polycondensation of the transesterification process. The retardant is added on completion of (3) and the retardant forms an energy barrier which is indicated by the dashed line. The energy barrier from the retardant alternates between the  $C-H$ ,  $C-C$  and  $C-O$  bonds. The end products show no reactivity between the formulated retardant and tuPOY

are attained and the reaction does not reverse towards the initial stage, resulting in Thermally Unstable Partially Oriented Yarns termed as **tuPOY**.

## 2.1 Production Process of tuPOY

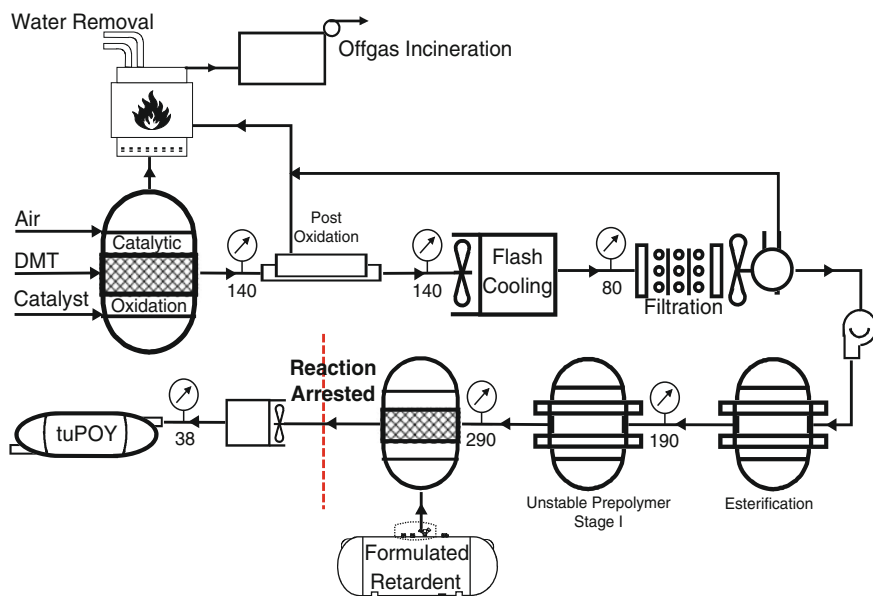
Esterification, transesterification and polycondensation forms the quintessence for polymerization of any synthetic polymer yarn [8–10]. Esterification reactions of polyester blends occur in the molten state via alcoholysis, acidolysis and direct interchange reactions. The exchange reaction results from alcoholysis between an ester<sup>1</sup> and an alcohol.<sup>2</sup> The acidolysis reactions involve carboxyl-terminated oligomers

<sup>1</sup>The ester used in our experiments is AR grade. Dimethyl terephthalate procured from MERCK chemicals

<sup>2</sup>The alcohol used in our experiments is XR grade. Ethylene Glycol procured from GlaxoSmithKline

formed during esterification while the transesterification proceeds via a direct interaction between carbohydroxyethoxy groups.

Esterification of DMT is the key initiation step in the industrial production of tuPOY. The complete process flow and instrumentation diagram for tuPOY is illustrated in Fig. 2.2. The DMT briquettes are oxidized at temperature of 140°C where the excess moisture is removed and the off gases are incinerated. The process of oxidation is followed by flash cooling and of the residue to obtain molten DMT. Esterification involves a reaction of molten DMT and EG stirred at 2000 r.p.m for over four hours. The repulsive nature of the hydrogen atoms in the alcohol initiates the esterification process at 190°C. This repulsive nature, causes the  $C - O$  bonds to break and the liberated hydroxyl group of EG combines with methoxy group of the ester as observed in reaction 1(A). This occurs because the  $C - C$  bond in ester is non-covalent and weak. Esterification entails the interchange of methoxy group in ester and the ethoxy group with the exoneration of methanol during the reaction. Reaction 1(A) results in the formation of an oligomer with carbomethoxy end group, and esterification process continues until all the alcohol is consumed. A similar exchange reaction occurs as observed in reaction 1(B). The esterification reactions in 1(A) and 1(B) illustrate the transformation of each methyl ester group on the DMT molecule into a hydroethoxyethyl ester group. The reaction progresses towards the transesterification stage with oligomers containing methoxy and hydroethoxy



**Fig. 2.2** Production process and instrumentation flow of tuPOY, showing arresting of the reaction at the polycondensation stage after transesterification. The final product is obtained at atmospheric temperature and pressure, retaining all the properties of synthetic partially oriented yarns

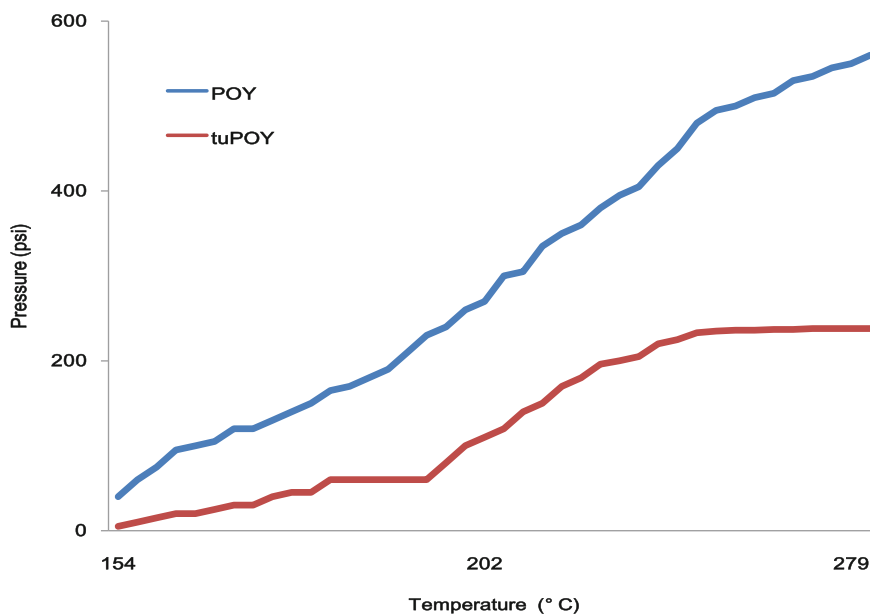
end groups. Esterification is ensued by transesterification of the carbomethoxy groups and condensation of the carbohydroethoxy groups. Transesterification and polycondensation reactions illustrated by reactions 2(a), 2(b) and 2(c) and 3 respectively result in the formation of linear oligomers of  $\beta$ -BHET family at temperatures of 290 °C. Transesterification reactions of carbohydroethoxy and carbomethoxy groups enter into 2(a) and 2(c) respectively while complex of transesterifications of carbomethoxy groups with oligomers containing carbohydroxyethoxy groups enter into reaction 2(b). Reaction 3 illustrates the complex of condensation reactions of the carbohydroxyethoxy groups. The retardant is added at the pre condensation level and reaction is allowed to arrest for about 4–5 hours. The retardant forms an energy barrier, indicated by the dashed line and the reaction is arrested at this point. The retardant prevents the linear BHET oligomers formed during transesterifications reaction to combine with each other, due to its energy barriers at the polymer chaining points. The barrier created by the retardant alternates between the bonds and the rings in BHET oligomers and hence prevents formation of any further polymer chains. The material thus arrested is in thermally unstable state and the reaction is prevented to complete the polycondensation stage. The effect of the retardant is not to change the properties of the regular POY but to stop the formation of polymeric chains which embed structural and chemical stability. The developed material is extracted at atmospheric temperature in molten form. It is then pressure extruded<sup>3</sup> and drawn out into fibers. The fiber produced during the process correlates with physical characteristics of raw of 78.2 [11–13].

## 2.2 Parametric Verification

tuPOY manufactured at the lab scale is vigilated by temperature and pressure changes measured concurrently at fiducial points in the process. Figure 2.3 shows a gradual increase in pressure (psi) with successively increasing temperatures, empirical during esterification. The contemporaneous plots which illustrate the pressure variations in the tuPOY lattice, with and without the presence of the retardant are illustrated. It is observed that the two curves run parallel, alongside each other during preliminary temperature variations. The similar morphology of the two plots, connotes the fact that tuPOY retains all the structural and chemical properties of the regular POY. However during transesterification, for identical temperatures, the pressure plot corresponding to tuPOY shows reduced psi in contrast with that observed in regular POY. The build up of an energy barrier, owing to the addition of the retardant in tuPOY, thwarts the pace of the reaction, thereby reducing the rate of increase in pressure.

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<sup>3</sup>Pressure extrusion to obtain a 78.2 denier tuPOY, is performed on a lab scale E10 from Oerlikon Barmag with a titer of 0.5–1.5 dpf. Further information can be obtained at <http://www.barmag-oerlikontextile.com/desktopdefault.aspx/tabid-431/>.



**Fig. 2.3** Parametric verification in the fabrication process of tuPOY. tuPOY progressively attains a steady state due to the action of the retardant

At the onset of polycondensation, the tuPOY curve progressively attains a steady state, while in the case of the regular POY the pressure gradually increases with temperature and the graph follows its normal course. The coordinates on the graph, where the pressure tends to approach a steady state value, indicate that the reaction is arrested at this point and the material is captured in its thermally unstable state.

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tuPOY: Thermally Unstable Partially Oriented Yarns  
Silicon of the Future

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