MOHSENI, SAMANEH. Role of Nucleating Agent in Nonwovens. (Under the direction of Dr. Behnam Pourdeyhimi and Dr. Eunkyoung Shim).

Nucleating agents are mostly used for developing polymeric materials through injection molding, blow molding, thermoforming and film formation processes. In these cases, polymers containing nucleating agents normally exhibit higher rate of crystallization and degree of crystallinity, improved electret, optical and physical properties. So, it is of interest to explore if similar important properties can be achieved in fibers and nonwovens by application of nucleating agents. However, the challenge is, those mentioned processes are different from the processes used for forming fibers and nonwovens. Therefore, in this research it is tried to investigate the effect of nucleating agent on morphology and mechanical properties of filaments as well as performance of nonwovens. In this regard, PP and 1,3,5-tris(2,2-dimethylpropionylamino) nucleating agent commercially known as Irgaclear XT-386 were used as materials. Material preparation was accomplished through two steps. First, nucleating agent and polymer was melt pre-compounded to produce PP/nucleating agent master batch with 10 wt. % concentration of nucleating agent. In the next step, PP was mixed with different amount of the PP/nucleating agent masterbatch and melt extruded through the Hills Homofilament line and Reicofil meltblown machine to produce melt spun filaments and meltblown nonwovens, respectively. To study crystallization behavior, crystallinity % and crystalline structure of samples, DSC, Modulated DSC (MDSC) and Wide Angle X-Ray Diffraction (WAXD) analysis were performed, respectively. While mechanical properties were evaluated with tensile testing machine and
filtration performance was tested by using TSI testing machine. Also the developed nonwovens structure and properties were evaluated.

Results showed application of Irgaclear XT 386 led to higher onset crystallization temperature and faster crystallization rate of polymer, higher elongation at break and toughness for the fibers. On the other hand with addition of Irgaclear XT 386 in meltblowing process, onset crystallization temperature of polymer increased which resulted in faster solidification of polymer melt and formation of bulkier structure nonwovens with higher air permeability and improved filtration properties. Moreover, increase of Die to Collector Distance (DCD) in meltblowing of polymer containing Irgaclear XT 386 resulted in change of crystalline structure, increase of crystallinity %, higher air permeability and lower solidity of webs, whereas increase of die air temperature led to change of crystalline structure, decrease of crystallinity %, lower air permeability and higher solidity of meltblown nonwovens.
© Copyright 2017 Samaneh Mohseni
All Rights Reserved
Role of Nucleating Agent in Nonwovens

by

Samaneh Mohseni

A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Fiber and Polymer Science

Raleigh, North Carolina

2017

APPROVED BY:

_______________________________  ________________________________
Dr. Behnam Pourdeyhimi          Dr. Eunkyoung Shim
Co- chair of Advisory Committee  Co- chair of Advisory Committee

_______________________________  ________________________________
Dr. Benoit Maze                  Dr. Saad Khan
DEDICATION

This dissertation is gratefully dedicated to my always encouraging ever faithful parents, my loving grandmas, my caring brother, Ali, my sweet aunt, Mahsan, and my brilliant supportive love, Mehdi.
BIOGRAPHY

Samaneh Mohseni was born in Babol, Mazandaran, Iran. She received her bachelor and master degrees, both in Chemical Engineering from Babol Noshirvani University of Technology, Babol, Iran in 2008 and 2012, respectively. After finishing her master, she started to work as a laboratory manager for a nonwoven company in conjunction with automotive industry for two years.

She joined The Nonwovens Institute (NWI), North Carolina State University in January 2014 to attend the PhD program in Fiber and Polymer Science. During her PhD, she investigated the role of nucleating agent in nonwovens and also obtained the graduate certificate in Nonwovens Science and Technology.
ACKNOWLEDGMENTS

I wish to express my sincere appreciation to all amazing people who helped and encouraged me throughout my PhD.

First, I would like to express my deepest appreciation to Dr. Eunkyoung Shim, for her kind support and advice throughout my PhD. Dr. Shim, you taught me to push my limits, work hard and always try to be the best version of myself. I learnt many incredible lessons from you! Thank you for everything!

Dr. Pourdeyhimi, one of the most incredible experience of my life was working in your amazing research group. I am so proud to be associated with you and continue to enjoy the privilege of being mentored by you. I am always fascinated with your hard work, kindness, thoughtfulness and optimism.

I am also very grateful to my committee members Dr. Saad Khan and Dr. Benoit Maze for their valuable comments and challenging questions which inspired me to think about my research from different aspects. I appreciate all the financial supports of The Nonwovens Institute (NWI) during the last 3 years and I am so honored to be part of this great institute. I would like to thank NWI staff who helped me during my PhD, especially, Amy Minton, Bruce Anderson, Dr. Loganathan Rangasamy, William Barnes, Eric Lawrence, Angelo Corino and Bradley Scroggins. I would like to express my gratefulness to my industrial advisors for their kind support and advice.

I am also very blessed and thankful to have my best friend, my husband Mehdi by my side for all these tough and challenging PhD years. Mehdi, you are the most caring and loving person that I had the luck to meet and love. You are the best!

Finally, many thanks to all the students at the NWI. You guys rock!
# TABLE OF CONTENTS

LIST OF TABLES.................................................................................................................. viii
LIST OF FIGURES.................................................................................................................. ix

1. Introduction......................................................................................................................... 1
  1.1 References....................................................................................................................... 4

2. Literature Review............................................................................................................... 5
  2.1 Crystallization.................................................................................................................. 5
    2.1.1 Nucleation................................................................................................................ 8
      2.1.1.1 Primary Nucleation............................................................................................ 10
      2.1.1.2 Secondary and Tertiary Nucleation.................................................................... 13
    2.1.2 Crystal Growth.......................................................................................................... 13
      2.1.2.1 Primary Crystallization..................................................................................... 14
      2.1.2.2 Secondary Crystallization............................................................................... 16
    2.1.3 Crystallization Rate of Polymers.............................................................................. 17
  2.2 Crystallization form a Quiescent Polymer Melt vs Crystallization during a Mechanical
  Deformation Process............................................................................................................ 20
    2.2.1 Crystallization during Meltblownng and Spunblowing Processes......................... 26
  2.3 Nucleating Agent........................................................................................................... 29
    2.3.1 Inorganic Nucleating Agents................................................................................... 31
    2.3.2 Polymers and Oligomers.......................................................................................... 32
    2.3.3 Organic Acid Derivatives (Early Developments)..................................................... 33
    2.3.4 Sorbitol Derivatives................................................................................................ 33
    2.3.5 Phosphorous-Containing Additives....................................................................... 35
    2.3.6 Organic Acid Derivatives (Later Developments).................................................... 35
    2.3.7 β-Nucleators.......................................................................................................... 37
    2.3.8 Nanoparticles......................................................................................................... 38
    2.3.9 Miscellaneous......................................................................................................... 39
  2.4 Nucleating Agents as Electret Additives....................................................................... 39
  2.5 Nucleating Agents Application in Crystallization from Quiescent Polymer Melt, Melt
  Spinning and Meltblowing Processes.................................................................................... 43
  2.6 References...................................................................................................................... 47

3. Effect of 1,3,5-tris(2,2-dimethylpropionylamino)benzene (Irgaclear XT 386) on
Crystallization and Crystalline Structure of Polypropylene Films........................................ 57
  3.1 Abstract ......................................................................................................................... 57
  3.2 Introduction .................................................................................................................... 57
  3.3 Materials and Methods.................................................................................................. 60
    3.3.1 Materials ................................................................................................................ 60
    3.3.2 Production of PP Film with Nucleating Agent........................................................ 60
    3.3.3 Differential Scanning Calorimetry Analysis............................................................ 60
    3.3.4 Wide-angle X-ray Diffraction Analysis (WAXD).................................................... 61
  3.4 Result and Discussion .................................................................................................... 61
    3.4.1 Differential Scanning Calorimetry Analysis............................................................. 61
    3.4.2 Crystalline structure ............................................................................................... 66
4. The Effect of 1,3,5-tris(2,2-dimethylpropionylamino)benzene (Irgaclear XT 386) on Crystalline Structure and Properties of Meltspun Polypropylene Fibers ........................................73
  4.1 Abstract ................................................................. 73
  4.2 Introduction .................................................................. 73
  4.3 Materials and Methods .................................................. 78
    4.3.1 Materials ............................................................. 78
    4.3.2 Production of Meltspun PP Fibers with Nucleating Agent ... 79
    4.3.3 Differential Scanning Calorimetry Analysis ...................... 79
    4.3.4 Isothermal Crystallization Analysis ............................... 80
    4.3.5 Wide-angle X-ray Diffraction Analysis (WAXD) ............... 80
    4.3.6 Single-Fiber Tensile Testing ..................................... 80
  4.4 Result and Discussion ................................................... 81
    4.4.1 Differential Scanning Calorimetry Analysis ...................... 81
    4.4.2 Crystalline structure ................................................ 88
    4.4.3 Single Fiber Tensile Properties ................................... 90
  4.5 Conclusion ................................................................. 93
  4.6 References ................................................................... 95

5. The Effect of 1,3,5-tris(2,2-dimethylpropionylamino)benzene on morphology and filtration performance of polypropylene meltblown nonwovens .........................98
  5.1 Abstract ..................................................................... 98
  5.2 Introduction .................................................................. 98
  5.3 Materials and Methods .................................................. 102
    5.3.1 Materials ............................................................. 102
    5.3.2 Production of Meltblown PP-Nucleating Agent Nonwovens Web .................. 103
    5.3.3 Differential Scanning Calorimetry Analysis ...................... 104
    5.3.4 Wide-angle X-ray Diffraction Analysis (WAXD) ............... 105
    5.3.5 Web properties ...................................................... 106
    5.3.6 Filtration Properties ............................................... 106
    5.3.7 Charging ................................................................ 107
  5.4 Result and Discussion ................................................... 107
    5.4.1 Differential Scanning Calorimetry (DSC) Analysis ................ 107
    5.4.2 Crystalline structure ................................................ 110
    5.4.3 Web Properties ...................................................... 112
    5.4.4 Filtration Properties ............................................... 115
  5.5 Conclusion ................................................................. 120
  5.6 References ................................................................... 121

6. The Structure-Property-Process Relationship in Nonwovens Containing 1,3,5-tris(2,2 dimethylpropionylamino)benzene ..............................................125
  6.1 Abstract ..................................................................... 125
  6.2 Introduction .................................................................. 126
  6.3 Materials and Methods .................................................. 129
    6.3.1 Materials ............................................................. 129
6.3.2 Production of PP-Nucleating agent Meltblown Nonwovens Web ......................129
6.3.3 Differential Scanning Calorimeter Analysis.....................................................131
6.3.4 Wide-angle X-ray Diffraction Analysis (WAXD)..............................................132
6.3.5 Web Properties..............................................................................................133
6.4 Result and Discussion .....................................................................................133
6.4.1 Effect of Die Air Temperature on PP Meltblown Webs Containing Irgaclea XT 386 .................................................................133
   6.4.1.1 Differential Scanning Calorimetry (DSC) Analysis ...............................133
   6.4.1.2 Crystalline Structure .............................................................................136
   6.4.1.3 Web Properties ......................................................................................138
6.4.2 Effect of Die to Collector Distance (DCD) on PP Meltblown Webs Containing Irgaclea XT 386 .................................................................142
   6.4.2.1 Differential Scanning Calorimeter (DSC) Analysis ...............................142
   6.4.2.2 Crystalline Structure .............................................................................144
   6.4.2.3 Web Properties ......................................................................................146
6.5 Conclusion ........................................................................................................150
6.6 References .......................................................................................................151

7. **Overall Conclusions and Recommendations for Future Work** ......................153
7.1 Overall Conclusion ..........................................................................................153
7.2 Recommendation for future .............................................................................154
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Onset crystallization temperature for PP films containing Irgaclear XT 386</td>
<td>63</td>
</tr>
<tr>
<td>3.2</td>
<td>DSC heating thermograms analysis of PP films containing different concentration of Irgaclear XT 386</td>
<td>65</td>
</tr>
<tr>
<td>3.3</td>
<td>Crystalline size of PP films containing different concentration of Irgaclear XT 386</td>
<td>68</td>
</tr>
<tr>
<td>4.1</td>
<td>Isothermal crystallization kinetic parameters for PP meltspun fibers containing Irgaclear XT 386</td>
<td>82</td>
</tr>
<tr>
<td>4.2</td>
<td>Isothermal crystallization kinetic parameters for PP meltspun fibers containing Irgaclear XT 386</td>
<td>84</td>
</tr>
<tr>
<td>4.3</td>
<td>DSC heating thermograms analysis of PP meltspun fibers containing Irgaclear XT 386</td>
<td>86</td>
</tr>
<tr>
<td>4.4</td>
<td>Crystallite size of PP meltspun fibers containing Irgaclear XT 386</td>
<td>89</td>
</tr>
<tr>
<td>5.1</td>
<td>Isothermal crystallization kinetic parameters of nonowvens containing Irgaclear XT 386</td>
<td>109</td>
</tr>
<tr>
<td>5.2</td>
<td>Crystallite size of PP meltblown nonwoven containing Irgaclear XT 386</td>
<td>112</td>
</tr>
<tr>
<td>6.1</td>
<td>The sample specification in investigating the effect of die air temperature in meltblowing of polymer containing Irgaclear XT 386</td>
<td>130</td>
</tr>
<tr>
<td>6.2</td>
<td>The sample specification in investigating the effect of DCD in meltblowing of polymer containing Irgaclear XT 386</td>
<td>131</td>
</tr>
<tr>
<td>6.3</td>
<td>Crystallite size of PP and PP meltblown nonwoven containing Irgaclear XT 386</td>
<td>137</td>
</tr>
<tr>
<td>6.4</td>
<td>Crystallite size of PP and PP meltblown nonwoven containing Irgaclear XT 386 at different DCDs</td>
<td>146</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2.1: Primary nucleation of polymer representation ........................................ 8
Figure 2.2: Schematic of nucleation rate and crystal growth vs temperature .................. 10
Figure 2.3: Lamellae growth in “a” and “b” directions .............................................. 14
Figure 2.4: Mechanism of chain segments lay down on the growing surface of the crystallite through (a) “tight fold with adjacent re-entry” and (b) the “chain segment independent deposition” ......................................................... 15
Figure 2.5: Schematic of shish-kebab structure model .............................................. 21
Figure 2.6: Image of polyethylene fibrillar crystal structure model ............................. 22
Figure 2.7: Schematic of meltblowing process ......................................................... 26
Figure 2.8: Schematic of the biax spunblown process (a) and picture of its die face (b) ...... 32
Figure 3.1: DSC cooling thermogram of PP films containing different concentration of Irgaclear XT 386 (crystallization exotherm) ....................................................... 62
Figure 3.2: DSC heating thermogram of PP films containing different concentration of Irgaclear XT 386 (melting endotherm) ......................................................... 64
Figure 3.3: The degree of crystallinity (%) of PP films containing different concentration of Irgaclear XT 386 ................................................................. 66
Figure 3.4: X-ray diffractogram of PP films containing different concentration of Irgaclear XT 386 ................................................................. 67
Figure 4.1: DSC cooling thermogram of PP melt spun fibers containing Irgaclear XT 386 (crystallization exotherm) ......................................................... 81
Figure 4.2: Non-isothermal crystallization of PP melt spun fibers containing Irgaclear XT 386 ................................................................. 83
Figure 4.3: Avrami plot of In (-In (1-Xt)) versus ln t for PP melt spun fibers containing Irgaclear XT 386 ................................................................. 85
Figure 4.4: DSC heating thermogram of PP melt spun fibers containing Irgaclear XT 386 (melting endotherm) ......................................................... 87
Figure 4.5: The degree of crystallinity (%) for PP melt spun fibers containing Irgaclear XT 386 ................................................................. 87
Figure 4.6: X-ray diffractogram of PP melt spun fibers containing Irgaclear XT 386 ........ 90
Figure 4.7: Single fiber tensile property of PP melt spun fibers containing Irgaclear XT 386 (elongation at break) ......................................................... 91
Figure 4.8: Single fiber tensile property of PP melt spun fibers containing Irgaclear XT 386 (tenacity) ......................................................... 92
Figure 4.9: Single fiber tensile property of PP melt spun fibers containing Irgaclear XT 386 (toughness) ......................................................... 92
Figure 5.1: Schematic of Ricofil meltblown machine .............................................. 104
Figure 5.2: DSC cooling thermogram of PP nonwovens containing Irgaclear XT 386 (crystallization exotherm) ......................................................... 108
Figure 5.3: The degree of crystallinity (%) of PP nonwovens containing Irgaclear XT 386 ................................................................. 110
Figure 5.4: X-ray diffractogram of PP meltblown nonwoven containing Irgaclear XT 386...
Figure 5.5: Effect of Irgaclear XT 386 on solidity of meltblown nonwovens
Figure 5.6: Effect of Irgaclear XT 386 on air permeability of meltblown nonwovens
Figure 5.8: Fiber diameter in meltblown nonwovens containing Irgaclear XT 386
Figure 5.9: Filtration efficiency versus pressure drop for pp control nonwoven and
nonwovens containing Irgaclear XT 386
Figure 5.10: Quality factors for pp control nonwoven and nonwovens containing Irgaclear
XT 386
Figure 5.11: Filtration efficiency versus pressure drop for pp control nonwoven and
nonwovens containing Irgaclear XT 386 before and after charging
Figure 5.12: Normalized charge retention efficiency for pp control nonwoven and
nonwovens containing Irgaclear XT 386 after 0, 0.5, 1 and 2 hrs. decay times
Figure 6.1: DSC cooling thermogram of PP meltblown nonwovens and PP meltblown
nonwovens containing Irgaclear XT 386 at different die air temperatures (crystallization
exotherm)
Figure 6.2: Crystallinity (%) of PP meltblown nonwovens and PP meltblown nonwovens
containing Irgaclear XT 386 at different die air temperatures
Figure 6.3: X-ray diffractogram of a) PP meltblown nonwoven and b) PP meltblown
nonwoven containing Irgaclear XT 386 at different die air temperatures
Figure 6.4: Effect of Irgaclear XT 386 and change of die air temperature on solidity of
meltblown nonwovens
Figure 6.5: Effect of Irgaclear XT 386 and change of die air temperature on air permeability
of meltblown nonwovens
Figure 6.6: a) Fibers in PP meltblown nonwoven, b) Fibers in PP meltblown nonwoven
containing 0.02 wt. % concentration of Irgaclear XT 386
Figure 6.7: Fiber diameter in meltblown nonwovens at different die air temperatures
Figure 6.8: DSC cooling thermogram of PP nonwovens and PP nonwovens containing
Irgaclear XT 386 at different DCDs (crystallization exotherm)
Figure 6.9: Crystallinity (%) of PP meltblown nonwoven and PP meltblown nonwoven
containing Irgaclear XT 386 at different DCDs
Figure 6.10: X-ray diffractogram of a) PP meltblown nonwoven and b) PP meltblown
nonwoven containing Irgaclear XT 386 at different DCDs
Figure 6.11: Effect of Irgaclear XT 386 and change of DCD on solidity of meltblown
nonwovens
Figure 6.12: Effect of Irgaclear XT 386 and change of DCD on air permeability of
meltblown nonwovens
Figure 6.13: a) Fibers in PP meltblown nonwoven, b) Fibers in PP meltblown nonwoven
containing Irgaclear XT 386
Figure 6.14: Fiber diameter of meltblown nonwovens at different DCDs
1. Introduction

Crystallization of the polymer as a physical transition of the material from disordered pattern molecules structure in a liquid phase to ordered one in a solid state, is rather more complex than the crystallization of low molar mass materials. Mechanical, thermal, chemical and optical properties of the developed polymeric products are highly influenced by the crystallization process. Due to chain connectivity, only limited crystallinity could be obtained through polymer crystallization. Nucleating additives are considered to facilitate crystallization process and change the properties and functionalities of polymers. Application of nucleating agent results in higher rate of crystallization and degree of crystallinity, higher thermal stability, improved electret, optical and physical properties of the developed polymeric materials. In fact, the morphology and crystalline structure of the products fashioned from crystallization of quiescent polymer melt differs significantly from the one developed upon crystallization under stress. In this regard, the effect of nucleating agent on the morphology and mechanical properties of materials developed under either of those conditions is anticipated to be different.

In the case of crystallization from the quiescent melt, where the polymer melt is cooled, effect of nucleating agent on crystallization behavior and material properties is a very well-studied topic. But, when it comes to crystallization under mechanical deformation such as meltspinning and meltblowing processes, where the polymer melt is co-currently cooled and extended, the crystallization process itself and the effect of nucleating agent has not yet been fully understood.
According to literature, nucleating agents are mostly used for developing polymeric materials through injection molding, blow molding, thermoforming and film formation processes. In these cases, polymers containing nucleating agents normally exhibit higher rate of crystallization and degree of crystallinity, improved electret, optical and physical properties. These properties are very important and interesting. So, it is of interest to explore if similar properties can be achieved in fibers and nonwovens by application of nucleating agents. However, the challenge is those mentioned processes are different from the processes involved in developing fibers and nonwovens. In this regard, the overall objective of this research is to investigate the effect of nucleating agent on morphology and mechanical properties of fibers as well as performance of nonwovens. Moreover, the structure-property-processing relationships of meltblown nonwovens containing nucleating agent and underlying mechanisms responsible for the behavior observed will be studied.

This document is organized in the following fashion.

Chapter 1 covers the introduction part. Chapter 2 is the literature review part which includes the important concepts including crystallization, nucleation, crystal growth and nucleating agent influence on different processing conditions. Besides, it explains different classes of nucleating agents and the ones used as electret additives. In chapter 3, the impact of 1,3,5-tris(2,2-dimethylpropionylamino)benzene (Irgaclear XT 386) on crystallization and crystalline structure of polypropylene films is explained.

In chapter 4, the effect of 1,3,5-tris(2,2-dimethylpropionylamino)benzene (Irgaclear XT 386) on crystalline structure and properties of meltspun polypropylene fibers is investigated.

Chapter 5 delivers the influence of 1,3,5-tris(2,2-dimethylpropionylamino)benzene on
morphology and filtration performance of polypropylene meltblown nonwovens. Chapter 6 covers the structure-property-processing relationship of nonwovens containing 1,3,5-tris(2,2-dimethylpropionylamino)benzene nucleating agent. Overall conclusions and recommendation for future are explained in chapter 7.
1.1 References


2. Literature Review

2.1 Crystallization

Crystallization of the polymer as a physical transition of the material from disordered pattern molecules structure in a liquid phase to ordered one in a solid state, is rather more complex than the crystallization of low molar mass materials \(^1,^2,^3\). Mechanical, thermal, chemical and optical properties of the developed polymeric products are highly influenced by the crystallization process \(^3\). Polymer crystallization process is classified into three different categories, including during polymerization crystallization, crystallization under stress and crystallization from a quiescent polymer melt \(^3\).

From the thermodynamic point of view, polymer crystallization happens when the crystalline state is more stable compared to the molten state, where the system will progress towards a low energy state \(^5\). Although, the crystallization process is limited by branches, side group interactions, chain entanglements and viscous drags on chains \(^5\). The direction of the crystallization process is governed by the change of Gibbs free energy according to equation \(^1\) \(^7\).

\[
\Delta G = \Delta H - T \Delta S
\]  

Where \(\Delta G\) is a change of the Gibbs free energy, \(\Delta H\) represents the change of enthalpy, \(T\) is an absolute temperature and \(\Delta S\) is a change of entropy.

Polymer melt crystallization is possible when the Gibbs free energy (\(\Delta G\)) is negative.

Upon cooling, as the temperature falls down and the change of entropy decreases, \(\Delta G\) becomes more negative, so crystallization is energetically more favorable.
Although, as the temperature falls down, the viscosity of the molten polymer increases which inhibits chain alignment and slows down molecular motions \(^5\). Rate of crystallization is also dominated by the magnitude of molecular reorganization mechanism and changes of Gibbs free energy \(^5\). For each crystallizable polymer, the crystalline and amorphous states are in equilibrium at a characteristic equilibrium melting temperature \(^5\). Below the equilibrium melting temperature, polymer crystallization starts, whereas above this temperature polymer remains at the molten state \(^5\).

In the case of super-cooled and super-saturated polymer melt in the absence of solid phase, concentration fluctuations result in creation of crystal phase \(^8\). This happens due to the decrease of temperature and is usually described in terms of nucleation and growth of nuclei that reached the critical cluster size \(^1,2\).

Any polymer can be crystallized if \(^9\):

- Polymer crystallization temperature falls below the melting temperature and above the glass transition temperature
- Nucleation occurs before crystallization
- Polymer molecular structure be sufficiently regular to provide crystalline ordering
- Rate of polymer crystallization be sufficiently high

Due to chain connectivity, only limited crystallinity could be obtained through polymer crystallization, so they are mostly referred to as semicrystalline materials \(^4\).

Different techniques can be used to evaluate crystallinity of semi-crystalline polymers. One method is employing dilatometry to measure the change of volume upon crystallization. Since polymer chains are densely packed in the crystalline state than in the molten state, the
difference in density and specific volume is expected \(^9\). Differential scanning calorimetry (DSC) also can be applied to determine the difference of heat capacity and/or enthalpy of fusion between the amorphous and crystalline states. Besides, X-ray scattering and Infrared and Raman spectroscopy are also applied to measure the crystallinity of semicrystalline polymers \(^9\). It is worth noting that, the degree of crystallinity is evaluated with respect to fully crystalline material \(^10\).

In crystallization process, partial alignment of the polymer molecular chain happens. Upon chains folding, polymer crystals called lamellae will be fashioned. These lamellae compose complex spherical macrostructures called spherulites \(^3\). In other words, spherulites contain lamellae and the amorphous regions between them \(^8\).

During crystallization process, the polymer melt is normally exposed to high pressure as well as shear which play important roles in crystallization behavior of the semicrystalline polymers \(^8\). For instance, when pressure increases polymer packs into highly dense crystals. Moreover, polymer melting point increases at higher pressure. For example, melting point of the PP increases from 170 °C at 0 bars to 190 °C at 500 bars. Furthermore, increase of pressure not only leads to formation of thicker lamellae but also extended chain crystals can be formed \(^4,8\).

Polymer crystallization happens via two major events, nucleation and crystal growth. Nucleation initiates crystallization process and once the fashioned nuclei reaches its critical cluster size, crystal growth starts.
2.1.1 Nucleation

The onset of phase change is identified as the creation of small particles of the new phase. When small particles formed, their interfacial energy ($\Delta G_{\text{surface}}$) will increase the total free energy. In other words, according to equation 2, total free energy is stated as the sum of phase transformation ($\Delta G_c$) energy and small particles interfacial energy ($\Delta G_{\text{surface}}$) \(^8\).

$$\Delta G = \Delta G_c + \Delta G_{\text{surface}} \quad (2)$$

The first term of this equation will become negative as the temperature falls below melting temperature, but the second term is always positive. Thermodynamically stable crystals can be obtained when the nucleus is formed through a path of positive $\Delta G$. As it is explained in figure 2.1, the critical nucleus can be fashioned once $\Delta G$ reaches to its maximum value. Once the crystal size gets larger than the critical cluster size at a negative value of $\Delta G$, the stable nucleus will be formed. At this point, since the primary nucleation has happened, the crystal growth is expected \(^8\).

![Diagram showing nucleation process](image)

**Figure 2.1**: Primary nucleation of polymer representation \(^8\)
Rate of nucleation can be determined according to nucleation and transport factors in terms of equation 3:\n\[
\frac{N}{N_0} = \exp \left( -\frac{E_D}{RT} \right) \cdot \exp \left( -\frac{\Delta G^*}{kT} \right)
\] (3)

Where,
N₀: A constant (when; E_D = 0 and ΔG = 0)
K: Boltzmann constant
E_D: Self-diffusion activation energy
ΔG*: Free energy for creation of critical size nucleus

Self-nucleation activation energy (E_D) depends on the glass transition temperature (T_g) of polymer. Moreover, ΔG*, the free energy required for the creation of critical size nuclei is not only a function of interfacial free energy, but also depends on the heat of fusion and super-cooling.\n
Rate of nucleation is highly influenced by the temperature. As it is shown in figure 2.2, during cooling, at the metastable region where polymer melt temperature is below the equilibrium melting point, rate of nuclei creation is very slow. This is due to the fact that, the created nuclei will dissolve in the polymer melt before crystal growth could even happen. By reducing the cooling temperature, the rate of nuclei formation will increase. However, upon further cooling of polymer melt, polymer viscosity increases, so rate of nuclei formation decreases till it becomes zero at the glass transition temperature.
Figure 2.2: Schematic of nucleation rate and crystal growth vs temperature

Polymer crystallization could be initiated via different types of nucleation including primary nucleation, secondary nucleation and tertiary nucleation.

2.1.1.1 Primary Nucleation

In the case of primary nucleation, four types of crystalline phase creation can be considered including spontaneous nucleation, orientation induced nucleation, auto-nucleation and heterogeneous nucleation.

Spontaneous (Homogeneous) Nucleation: This type of nucleation happens due to supercooling or supersaturation. If random molecular motions that occur in polymer melt lead to the alignment of an adequate number of chain segments, the stable ordered phase
called nucleus would be created. This unique crystalline phase initiation is referred to as spontaneous (homogeneous) nucleation. As the process temperature decreases, rate of polymer nucleation increases. Rate of homogeneous nucleation is also affected by the molecular orientation of the polymer melt. As the molecular orientation of the polymer melt increases, entropy difference between the crystalline state and the molten state decreases, so rate of homogeneous nucleation increases.

**Orientation-induced nucleation:** This type of nucleation occurs due to some degree of polymer molecular alignments which leads to the decrease of difference between crystalline and liquid’s molecules arrangement. Orientation-induced nucleation plays an important role in processing of the semi-crystalline polymers, especially where polymers are sheared during the process.

**Autonucleation:** This type of nucleation refers to initiation of nucleation from incompletely melted crystalline phase present in the polymer melt. Autonucleation mainly occurs through thermal analysis studies of polymer.

**Heterogeneous nucleation:** Foreign nuclei such as certain types of contaminants in the polymer melt are considered as heterogeneous nuclei. Contaminant act as a pre-existing surface area that reduces the energy barrier for creation of the stable nucleus and initiation of nucleation. The foreign phase can be an accidental contamination, nucleating additives, and an external substrate. Accidental contamination is mainly caused by the presence of more or less well-dispersed materials and/or residues during the initial manufacturing of the polymer, chain defect, chain branching and chain end-groups. An external substrate mainly added during polymer lamination, injection molding and fiber reinforcing processes, induces
polymer nucleation through the creation of large number of small crystals in the final developed material. Nucleating additives, that have surface periodicities which match the length of polymer unit cell are considered as the most effective foreign nuclei. Nucleating agents are added to the polymer melt to improve the crystallization rate and degree of crystallinity. Application of very low concentration of nucleating agent results in higher thermal stability, improved electret, optical and physical properties of the developed polymeric material.

As it is noticed, heterogeneous nucleation refers to nucleation at the interface with the pre-existing foreign surface. So, in presence of the foreign surface, free energy against the primary nucleation ($\Delta G_H$) decreases which leads to the increase of nucleation as well as the overall rate of crystallization.

Primary nucleation ($\Delta G_H$) is expressed as:

$$\Delta G_H = 16 \cdot \Delta \gamma \cdot \gamma_e \cdot T_m^2 / (\Delta H \cdot \Delta T \cdot \rho_c)^2$$  \hspace{1cm} (4)

Where, $\Delta \gamma$ is the difference parameter for an interfacial free energy of the surface contacting the melt and the other one contacting the foreign nucleus. $\gamma$ represents side surface free energy. Supercooling and difference parameter of specific interfacial energy play important roles during polymer heterogeneous nucleation. Free energy of heterogeneous nucleation is inversely proportional to $1/\Delta T^2$, so supercooling extremely affects polymer nucleation rate. Moreover, with decrease of the difference parameter of specific interfacial energy, the free energy against nucleation will become smaller which is in favor of the nucleation process.
2.1.1.2 Secondary and Tertiary Nucleation

In secondary nucleation, polymer chain crystallization occurs on surface of the flat polymer crystal\(^8\). Tertiary nucleation refers to crystallization of polymer at the edge of the polymer crystal\(^9\).

2.1.2 Crystal Growth

Semi-crystalline polymer crystal growth is known as a secondary nucleation which occurs on the growing face of an existing nucleus. The linear crystal growth rate is defined in terms of equation 5 as follows\(^8\):

\[
\frac{G}{G_0} = \exp \left( -\frac{E_D}{RT} \right) \cdot \exp \left( \frac{\Delta G^*}{KT} \right)
\]

(5)

Where \(G_0\) represents a constant for \(E_D = 0\) and \(\Delta G^* = 0\).

Crystal growth is directly affected by crystallization temperature. In other words, when temperature decreases below the melting point, crystal growth rate increases and reaches to its maximum value at \(T_K \approx 0.5 \left( T_m^0 + T_g \right)\)\(^8\). However, below \(T_k\), rate of crystal growth decreases. Crystal growth rate is also influenced by molecular weight as well as the molecular weight distribution\(^8\). According to a published study, for PP, rate of crystal growth decreased as the molecular weight increased. Nucleation rate increased at the lower molecular weight and broader molecular weight distribution\(^{13}\). In the case of PET, by increasing the molecular weight, rate of crystallization decreased\(^{14}\). Incorporation of comonomers into the polymer chain reduces the crystallization rate. In fact, with addition of comonomers, crystal structure would be disrupted and crystallization would be harder which eventually leads to lower crystallization rate and crystallinity\(^8\).


2.1.2.1 Primary Crystallization

Deposition of chain segments from a polymer melt with a temperature below the equilibrium melting temperature on the surface of an existing polymer crystallite or a nucleus is considered as the primary crystallization. As it is illustrated in figure 2.3, primary crystal growth occurs relative to the unit cell in “a” and “b” directions. Obviously, the lamellae tends to grow faster in either “a” or “b” direction which is thermodynamically more favored. Moreover, since the crystallite thickness depends on crystallization temperature, so at certain crystallization temperature, the crystallite thickness in c direction remains constant.

![Figure 2.3: Lamellae growth in “a” and “b” directions](image)

As it is shown in figure 2.4, primary crystal growth can take place via two different types of molecular rearrangement including “tight fold adjacent re-entry” or “independent deposition of chain segment”. In the case of “tight fold adjacent re-entry”, chains are “reeled in” from polymer melt on the surface of an existing polymer crystallite. For this type of chain segment deposition mechanism, several orders of magnitude faster molecular motion
along a chain’s contour length than the crystal growth rate is required. When it comes to “independent deposition of chain segment”, only local chain motion is required for each chain segment to align itself with the face of the pre-existing crystallite. In practice, a combination of both mechanisms can take place. For crystallization at lower temperatures, “independent deposition of chain segment” is more likely to occur. While, “Adjacent re-entry” will be dominated at higher crystallization temperatures. When it comes to industrial processing of polymers, primary crystallization will be completed in a few second to a minute or two.

Figure 2.4: Mechanism of chain segments lay down on the growing surface of the crystallite through (a) “tight fold with adjacent re-entry” and (b) the “chain segment independent deposition”.
2.1.2.2 Secondary Crystallization

After primary crystallization, the polymer will experience a thermodynamically metastable phase. So, further crystallization is favored energetically. However, fashioned crystallites are surrounded by amorphous regions and further crystallization is restricted due to limited molecular motion in the amorphous region. However, after a period of time and re-arrangement of the molecular segment of the amorphous region, further crystallization and crystal growth are likely to happen via a process recognized as secondary crystallization. Thickening of available fashioned crystallites and creation of new crystallites which may continue for hours, days or weeks is known as secondary crystallization.

Thickening of crystallites is possible through alignment of chain segments in the amorphous region next to the existing crystallite surfaces. In other words, chain segments of amorphous regions re-organize themselves beside the existing polymer crystallite to create additional crystalline unit cells. In this regard, crystallites thickness in “c” dimension will be increased. Alignment of chain segments of the amorphous phase between the pre-fashioned crystallites leads to the formation of new crystallites which is considered as a secondary crystallization. The new-fashioned crystallites are smaller in a, b and c dimensions comparing to the primary crystallites. Secondary crystallization mostly occurs in the case of quench cooling of polymers. In fact, quench cooled polymers crystallinity (%) is low and polymers contain rather large volumes of the amorphous region. The rubbery amorphous region is required for the secondary crystallization to be initiated. The volume of crystallinity formed upon secondary crystallization is less than 10% of the volume of the crystallinity obtained from primary crystallization.
2.1.3 Crystallization Rate of Polymers

In general, factors which increase the difference of free energy between the crystalline and amorphous phases as well as ones that stimulate re-alignment of chain segments in the amorphous region, lead to increase in polymers crystallization rate. These factors include external conditions and molecular characteristics. External conditions include heterogeneous nucleation, temperature and molecular orientation. Molecular characteristics contain chemical structure, copolymer composition, molecular weight, molecular weight distribution, stereoregularity and long chain branching.

The strongest driving force of crystallization process for simple chemical composition polymer is the enthalpy difference between the crystalline and amorphous phases. In fact, when the enthalpy of crystalline and amorphous states differs significantly, then the Gibbs free energy becomes more negative and driving force of the crystallization process will increase consequently. In this regard, polyethylene, due to its simpler chemical composition than that of the polypropylene, crystallizes more readily. Moreover, certain stereoregular forms of molecular arrangements lead to easier and faster crystallization. For instance, isotactic PP due to its simpler unit cell crystallizes faster comparing to syndiotactic PP.

Copolymers crystallization rate is slower than homopolymers because comonomer decreases the enthalpy difference between the crystalline and the molten states. Also, the average length of crystallizable monomer sequences is limited by comonomers. In this regard, participation of these monomers takes place in smaller crystallites which are unstable at the lower temperature and for more viscose polymers. Stereodefects also reduces the crystallization temperature and average length of crystallizable monomer sequences.
Moreover, alignment of the crystallizable monomer sequences would be blocked by non-crystallizable monomer sequences. Minor comonomers that are larger than the major comonomers will act as anchors that restrict the slippage of chains. Likewise, in the case of high molecular weight and narrow molecular weight distribution, viscosity of polymer melt increases which limits the crystallization. In the case of flexible polymers, easier molecular reorganization leads to higher rate of crystallization. Polymers with a double bond and ring structure in their backbone showed less flexibility and consequently lower rate of crystallization.

Temperature as an external factor highly affects polymer crystallization rate. As the temperature of the molten polymer falls lower than the equilibrium melting temperature, nucleation is more likely to happen and rate of crystallization increases. However, at lower temperatures, polymer viscosity increases, and crystallization rate decreases consequently. In fact, highest crystallization rate occurs at approximately mid-way of the polymer glass transition temperature and equilibrium melting temperature.

Polymer molecular orientation results in higher rate of crystallization. This phenomenon is attributed to the reduction of the entropic difference between the crystalline and molten states and increase in the possibility of formation of suitably aligned chain segments to create a nucleus.

The overall crystallization rate is dominated by nucleation and crystal growth which usually is defined at a given temperature as an inverse of time required to reach one-half of the fully crystalline polymer ($1/t_{1/2}$).
Depending on different types of crystallization including isothermal crystallization and constant cooling rate crystallization, different definitions can be used to explain polymer crystallinity development as a function of time.  

In case of isothermal crystallization through which polymer melt is kept at the same temperature, polymer crystallinity development could be defined with Avrami equation:

\[ X_c(t) = 1 - \exp(-K. t^n) \]  

(6)

Where \( X_c(t) \) is the relative crystallinity at time \( t \) and \( n \) is the Avrami exponent related to the nucleation mechanism and crystal growth geometry.

In equation 6, \( K \) as the Avrami rate constant governs both nucleation and crystal growth parameters. In the case of linear rate growth (spherically symmetric) of polymer crystals as well as heterogeneous nucleation, \( n \) is considered as 3.

For constant cooling rate crystallization, where the polymer melt is cooled at a constant rate, Ozawa equation can be applied as follows:

\[ X_c(t) = 1 - \exp(-K (T)/\phi n) \]  

(7)

Where \( K (T) \) represents the Ozawa rate constant and \( \phi \) stands for the constant cooling rate (-\( \delta T/\delta t \)).

According to published study by Hieber, Avrami equation could be linked to Ozawa equation by Nakamura equation. Therefore, when a system undergoes both isothermal and non-isothermal conditions, crystallization kinetic of this realistic process can be predicted according to Nakamura equation.
2.2 Crystallization form a Quiescent Polymer Melt vs Crystallization during a Mechanical Deformation Process

Upon slowly cooling the quiescent polymer melt below its melting temperature, crystallization happens via nucleation and crystal growth. Lamella as a secondary structure will be fashioned consequently. Lamellae is a region of closely packed chain segments and contains tight folding primary chains or more forgiving switchboard reentry arrangement. Regions between lamella are considered as amorphous regions. Further crystal growth leads to the formation of ribbon-like strips from larger lamellae.

Upon branching, twisting, stacking and folding together, ribbon-like strips are able to form large size (tens of microns) tertiary structures called spherulites. Enveloping the entire volume, spheres of growing crystals met each other and straight or curved boundaries will be formed. In this case, crystallinity is quite high; however, presence of amorphous regions between the lamellae results in absence of long range order and lack of directional strength.

In the melt-spinning process, crystallization plays an important role in developing final products. Fibers are developed under extreme molecular orientation and driving forces. The presence of crystals in semicrystalline synthetic fiber structure is necessary to avoid shrinkage under different conditions (e.g. cleaning) and to provide required strength and stiffness. In the melt-spinning process where the volume element is co-currently cooled and extended, crystallization process is governed by super cooling and stress. Here, the first step of crystallization which happens though ordering of the polymer chains in a side-by-side structure is similar to crystallization from a quiescent melt. But when it comes to higher order structures, crystallization shares few characteristics with spherulites. In this
regard, at least, two common morphologies including shish-kebab and microfibril structures are expected \(^8, 20, 22\).

Shish-kebab structure implies the backbone analogous to the shish and lamellar crystals to the kebab. The schematic of shish-kebab structure is shown in figure 2.5. In this structure chain extension results in entropic reduction. So, it is quite expected that backbone parallel chains crystallize first and serve as the nucleating sites for future lamellae formation.

![Schematic of shish-kebab structure model](image)

**Figure 2.5**: Schematic of shish-kebab structure model \(^{22}\)

It is reported that melt-spun polypropylene fibers adopt the shish-kebab structure \(^{23}\). Since tensile modulus of such structures is very high, fashioned fibers show good strength characteristics. Microfibril is another crystalline superstructure fashions during a melt-spinning process, however, shish kebob structure is also a type of microfibril crystalline structure.
The microfibril structure is consist of long and narrow stacks of lamellae with the uniform diameter along its length \(^{20}\). Formation of microfibril crystalline structure in a melt-spun polymer may be related to the kinetics of crystallization. For instance, during fiber spinning of polyethylene terephthalate as a slow crystallizing polymer, microfibril structure is a dominant fashioned structure. Figure of polyethylene fibrillar crystal structure model is shown in figure 2.6.

![Image of polyethylene fibrillar crystal structure model](image)

**Figure 2.6** : Image of polyethylene fibrillar crystal structure model \(^{24}\)

During the melt-spinning process, polymer melt leaves the spinneret and is cooled and drawn mechanically by a reel whose take up velocity is a few hundred to thousand meters per minute \(^{20}\). In this regard, orientation of the polymer molecules increases which act as a large driving force for crystallization process to be initiated. At low and intermediate take up velocities, since the driving force is not large enough, relaxation of polymer chains occur before the crystallization can happen \(^{20}\).
So, the developed fiber has intermediate orientation with no or very low degree of crystallinity. In this case, crystallization probably can be influenced by nucleating agents. However at high take up velocities rate of chain stretching is much higher comparing to relaxation which leads to crystallization in the spinline. Because of reduction of entropy for the extended chain in noncrystalline regions and consequently increase of melting point, crystallization rate during melt spinning of commercial fiber is quite high. In fact, undercooling of the quiescent system would be lower than that of oriented noncrystalline system. So crystallization rate of oriented fiber should be very high since relaxation will not occur in this case.

Many research have been conducted on PET fibers as a primary material for commercial fibers. It was shown that in melt-spinning of PET fibers the applied stress is 3-4 orders of magnitude larger comparing to the quiescent conditions. Therefore, it is expected that in the highly oriented PET crystalline structure, crystallization can occur very rapid. However, there is always a competition between relaxation and crystallization. At low extension rates the volume element chains relaxation happens and crystallization will not occur. But at higher spinning speeds, little relaxation takes place before the occurrence of crystallization or frizzed oriented amorphous phase. In fact, either crystalline or frozen amorphous states formation highly depends on the absolute rate of crystallization as well as the time available for the transition to happen. In practice, high spinning speed is required not only to outstrip the relaxation but also to achieve some degree of crystallinity before reaching the glass transition temperature.
When it comes to heat treatment of intermediate spinning speed spun fibers, competition between relaxation and crystallization is inevitable. At low tensions, relaxation of chains happens before crystallization can take place. Thus, the rate of drawing plays an important role on the degree of crystallinity of the produced fiber.

For PET (the slow crystallizing polymer) and Nylon 6, crystallization during spinning is not possible unless the critical take-up velocity of 3000-4000 m/min is reached. This can be related to the competition between relaxation and crystallization during crystallization process.

For the fast crystallizing polymers like polypropylene, development of crystallinity in the spinline was studied employing WAXS and SAXS techniques. According to online studies, for crystallization in the spinline of fast crystallizing polymers, as the distance from the spinneret increases, the interplanar spacing of the crystalline decreases and at the same time crystallinity increases. Since crystals defects always tend to expand the crystal lattice, it can be stated that the initially fashioned crystals are defective. But crystals perfection increase as the crystallinity increases. It is consistent with the concept that low mobility of materials, as well as short time available for the crystallization process, lead to incorporation of initial crystals in significant defect levels.

Online spinline crystallization studies at low take up speeds have been performed on polymers including polypropylene, nylon 6, PET, poly (vinylidene fluoride), polybutene-1, nylon 66 and poly (ethylene naphtalate). Results suggested that crystallization in the spinline is more likely to happen at high spinning speeds which are related to the formation of the neck in fibers and other effects associated with high spinning speeds. Moreover, fashioned
crystalline structure may stay at nonequilibrium state and superstructure of the spun fibers seems to shape as microfibrillar.

Until recently there is no general agreement on how crystallinity develops in the spinline. Majority of studies state that, the crystallization phenomenon in the spinline can be described based on nucleation and growth that has been challenged with spinodal decomposition theory, recently. In this regard, Ziabicki, Jarecki, and George investigations suggested that nucleation should be profuse for high spinning speed processes in the presence of large driving force. For crystallization at high spinning speed, George described that due to absence of activation barrier for nucleation, nucleation would be an instantaneous phenomenon \(^\text{20}\). At low spinning speeds, since the driving force is not large enough, the developed fiber has intermediate orientation with no or very low degree of crystallinity. In this case, crystallization probably can be influenced by nucleating agents \(^\text{25,26}\). Application of nucleating agent for crystallization from both quiescent iPP melt and meltspinning processes results in higher degree of crystallinity and onset crystallization temperature of the developed materials \(^\text{26}\). However, in the case of melt spinning process, nucleating agent influence is more pronounced at low spinning speeds \(^\text{26}\). At higher spinline stress, rate of crystallization is very high and effect of nucleating agent would not be very impressive, although it is not completely eliminated \(^\text{26,27}\). With addition of nucleating agent, crystallization tends to occur at a higher temperature closer to the spinneret, where the molecular orientation is lower in the melt so lower orientation for the product is expected \(^\text{26}\). In this regard, decrease of modulus is quite possible due to reduction of molecular orientation, even though higher degree of crystallinity can be obtained in presence of nucleating agent \(^\text{25,27}\). Reduction of molecular
orientation in presence of nucleating agent may lead to higher elongation of the developed fibers.

2.2.1 Crystallization during Meltblowing and Spunblowing Processes

Meltblowing technology is a one-step nonwoven manufacturing process, which governs continual production of fine fibers to form self-bonded fine fibrous webs. Any thermoplastic polymer can be used for meltblowing process, however, PP is the most commonly used one. The schematic diagram of the meltblowing process is illustrated in figure 2.7.

![Schematic of meltblowing process](image)

*Figure 2.7: Schematic of meltblowing process*

When it comes to high throughput processes for the production of fine fibers of 1-5 μm size diameter, meltblowing is the preferred technology. Melblown fibers might be finer than the spunlaid fibers, however they are usually weaker. In meltblowing, fiber attenuation
occurs very close to the die face, so crystals are formed randomly. In this regard, low crystallinity and crystal orientation will be obtained. But, during melt-spinning, first, fibers are exposed to cool quench air and then they will be attenuated by high-speed air and drawn by rollers. Crystalline microfibrils which impart strength to fibers, form upon extensive drawing at low temperatures. In this case, nucleation and growth of crystals happen and microfibril or shish kebob structures will be obtained.

During meltblowing process, fiber attenuation occurs close to the die face, so mechanical elongation and crystallization will not occur at the same time. For instance, PP fibers may not be fully crystallized until they reach the collector. According to in-line x-ray scattering studies, polymer crystallization does not happen unless it reaches > 20 cm distance from the die face. Moreover, according to x-ray analysis, meltblown fibers are contained fine fibers consist of glassy state and coarse fibers consist of large spherulites. In fact, since fine fibers surface area to volume ratio is higher than the one in coarse fibers, so they are cooled faster and are quenched into the glassy state. However, the glassy state is not stable and at temperatures lower than the melting point, they will transform to spherulite crystalline structure. Although, at room temperature they will remain at glassy state. Neither of coarse fibers nor fine fibers showed high crystallinity, crystal orientation, and high tensile strength.

Spun-blown system is a unique meltblowing technology, where there are air outlets around each spinneret. In this regard, the main difference in mechanism between spunblown and meltblowing is aerodynamic of the process. In the case of meltblowing system, air flow usually impinges immediately on the extruding polymer while in spun blown system there is
a gap between the inner and outer spinneret diameter which inhibits such interaction for perhaps a few hundred microns. In fact, the popularity of this process is because of using less air flow than the conventional meltblowing system, yet providing fine fibers. The schematic of the biax spunblown process and a picture of its die face are shown in figure 2.8. The spunblown system is not a well-studied technology and crystalline structure of the spun-blown fiber is not known thoroughly.

Figure 2.8: Schematic of the biax spunblown process (a) and picture of its die face (b)³²,³³
As it is known, shish kebob or microfibril structures can be formed at low temperature and under drawing. The spunblowing system produces fine fibers which are fashioned in the central dies where temperature remains high for a longer time which leads to greater attenuation consequently. If it is assumed that, the finer fibers are the most insulated ones, so fibers cooling rate can be sufficiently slow and spherulite nucleation and growth can happen. Moreover, coarse fibers can be quenched into the glassy state through interaction with the secondary airflow and be cooled rapidly.

2.3 Nucleating Agent

Nucleating agents can be applied to polymers which crystal growth rate is neither too high nor too low 8. For instance, HDPE crystal growth is extremely high that addition of nucleating agent will not affect crystallization rate 6. The reason is, as soon as the nuclei fashion, crystals growth occurs extremely fast. In this regard, PP with an intermediate crystal growth rate can be nucleated easily 8.

In general, application of nucleating agent for semicrystalline polymers leads to two main phenomena including an increase in overall rate of crystallization and decrease of average spherulites size 15, 28. As the overall rate of crystallization increases, polymer will solidify faster which leads to decrease of process cycle time and consequently all other commercial advantages 6, 28. Also, spherulites sizes are reduced upon application of nucleating agent in the polymer. In this regard, mechanical properties such as tensile strength and hardness and optical properties like clarity will be affected as well 36.
By application of some types of nucleating agents, the fashioned polymeric product will have smaller crystal size that wavelength of visible light can pass through them and clarity of the product will be increased consequently. Nucleating agents which provide high transparency are referred to as clarifying agents. Due to the commercial advantages and its moderate crystal growth rate, PP is the most commonly used polymer in research and industry to investigate the effect of the nucleating agent on polymers.

Two physically different classes of nucleating agent used for PP include particulate and soluble systems. In the case of particulate systems, the classical dispersion mechanism is dominant where particle size and polarity difference between polymer and additive are critical. Additives including talc, organophosphate, and sodium benzoate belong to the category of particulate nucleating agent. In a soluble system, the degree of dispersion is dominated by the sequence of dissolution upon heating and recrystallization upon cooling. In this case, nucleation efficiency is dominated by polarity difference as well as the shape of fashioned crystals. Sorbitol derivatives and benzene trisamides belong to this category of nucleating agents. Also, nucleating agents regarding their chemical structures can be classified into two different categories including organic nucleating agents such as organophosphate, trisiamide and sorbitol derivatives and inorganic ones like calcium carbonate, talc and magnesium hydroxide.

As it is known, PP is commercially available in three different forms including isotactic, syndiotactic and atactic with different degrees of tacticity. Among them the isotactic form is the most common used one. Isotactic PP as a polymorphic material is characterized by
different crystal forms including α (monoclinic), β (trigonal), γ (orthorhombic) and mesomorphic (smetic). In this regard nucleating agents used for different modifications of PP are categorized as:

- Nucleating agent for α- and γ- polypropylene
- Nucleating agent for β- polypropylene

Another more in detail classification of different types of nucleating agent includes:

- Inorganic nucleating agents
- Polymer and oligomers
- Organic acid derivatives (early developments)
- Sorbitol derivatives
- Phosphorous containing additives
- Organic acid derivatives (later developments)
- β nucleating agents
- Nanoparticles
- Miscellaneous

2.3.1 Inorganic Nucleating Agents

Minerals including talc, diatomite, silica, wollastonite and mica are known as inorganic nucleating agents. These additives not only improve mechanical properties and flame retardancy but also reduce the warpage and shrinkage of the final polymeric products. Moreover, these additives are sometimes able to induce β- crystalline form of PP and consequently improve mechanical properties of materials. Nanocomposites are also
categorized as useful inorganic nucleating agent but talc, mica, and wollastonite are applied as the three main inorganic additives for PP \(^{41}\).

Reinforcement and nucleating effect of these additives highly depend on additive surface treatment, concentration, particle shape, size and distribution \(^{42}\). Assuming Tc as a reference, the nucleating effect of talc > wollastonite > mica \(^{43}\). It is also stated that, the presence of 5 wt. % concentration of talc leads to 40% increase in nucleation efficiency \(^{43}\). For PP systems containing talc, free energy as a thermodynamic barrier to form a new crystallite is much lower than the pure PP \(^{38}\). In this regard, in the presence of talc, new crystallite phase can be fashioned easier compared to pure PP system \(^{38}\). Inorganic nucleating agent’s advantages include their abundancy, low price and improvement in mechanical properties and etc. \(^{11,30}\). However, problems related to fracture and particle distribution of mineral additives are limiting factors and somehow they are superseded by later developed nucleating agents \(^{11,30}\).

2.3.2 Polymers and Oligomers

Different polymers have been used as nucleating agent in early patents. High-density-polyethylene (HDPE) was utilized as the nucleating agent for low-density polyethylene (LDPE) while PP was applied for polyamide and poly alkanate tipene (PAT) \(^{44}\). In both cases, nucleation efficiency was lower compared to the later developments \(^{44}\). Different polymer matrix/polymer additive have been discovered which provided better nucleation efficiency. Among them Polypropylene/ polyvinylcyclohexane and polylactic acid/ stereocomplex systems were the most interesting pairs \(^{6}\).

Moreover, different oligomeric species were developed and used as nucleating agents such as PP with 2,6,10,15,19,23-hexamethyltetracosane and polyethylene therphetalate (PET) with
oligo- PET salts \(^6\). These species recovery from polymer is not practically feasible which limits their application as nucleating agents \(^6\).

2.3.3 Organic Acid Derivatives (Early Developments)

Inorganics and hydrocarbons used as nucleating agent did not provide high nucleation efficiency \(^6\). In this regard, organic acid derivatives especially salts have been introduced as more effective nucleating agents \(^6\). Among early developed organic acids, benzoic acids and p-t-butylbenzoic acid showed low and intermediate nucleating efficiency, respectively \(^6,38\). Sodium salts such as cycloaliphatic carboxylates act as effective nucleating agents. However, sodium salt of aliphatic dicarboxylic acids is not effective except the granulated and succinated ones \(^6\). Sodium benzoate is the most common commercially applied acid salt, however, it is somewhat overtaken by other developed nucleating agents. To provide a good nucleation efficiency, sodium salt should be very fine \(^6\). Another difficulty is, sodium benzoate cannot be dispersed in the polymer easily, however dispersing aids such as zeolites and nanoparticles of alumina coated silica can be used to overcome this problem \(^45\), \(^46\). Heterocyclic acids, imido acid salts and amine-sulfonate salts are also applied as organic acid nucleating agents \(^6\).

2.3.4 Sorbitol Derivatives

Sugars such as fructose and sucrose have been used as nucleating agents for years. Sugar alcohol derivatives such as sorbitol and xylitol are also applied as nucleating agents \(^47\). The reaction of sorbitol and aldehydes results in the formation of mon-, di- or tri-acetals 1,3:2,4-Dibenzylidene sorbitol (DBS) \(^48\). These products were developed and used as gelling agents
for cosmetic and pharmaceuticals for years \(^{48}\). It was also soon considered that these additives can act as nucleating agents for polyolefins, particularly PP \(^{6}\).

DBS has a butterfly shape with a polar sugar body and hydrocarbon wings which provide nucleating sites upon forming a physical gel in the matrix before crystallization \(^{6,38}\). It is also stated that DBS has two unreacted hydroxyl groups in its inter- and intra-molecular bonds \(^{6}\). This can lead to molecular agglomeration and consequently stability of the fashioned structure in the PP matrix. Monobenzylidene sorbitol provides gel structure; however, it crystallizes to individual spherulites very soon. Tribenzylidene sorbitol appears to give no gelation instead provides needle-like crystals \(^{6}\). It is proposed that nucleation efficiency of DBS > monobenzylidene sorbitol (MBS) > tribenzylidene sorbitol (TBS) \(^{6}\). Studies suggested that upon cooling of DBS containing system, the additive agglomerates, and 3D homogeneous microfibrillar structure will be formed \(^{49}\). Upon further reduction of temperature these fibrils crystallize and provide nucleating sites for crystallization \(^{49}\). The formed gel allows a uniform distribution and creation of a huge number of very small crystals which are smaller than the wavelength of visible light. So wavelength of visible light can pass through them and high degree of clarification is obtained for the developed polymeric materials. According to aforementioned facts, DBS is also known as clarifying agent \(^{50,51}\). Although DBS provided the high nucleating efficiency but it was rapidly substituted by more efficient nucleating agents developed with the reaction of substituted benzaldehydes and sorbitol such as bis (4-methylbenzylolated) sorbitol and bis (3,4-dimethylbenzylidene) sorbitol \(^{49}\).
Mixtures of different types of DBS also can be applied as nucleating agents. Depending on different combinations, synergic nucleation performance, enhanced stability and the more economic combination can be obtained. DBS types nucleating agent also can be combined with other types of the nucleating agent such as polymers, bicyclic carboxylates and talc. Despite the good performance of DBS type nucleating agent and its substituents, due to their sugar based chemistry, they are not thermally and chemically stable, especially in presence of acids, where additive decomposition can happen. However, some materials can be added to improve thermal stability such as sorbic acid salts, sulfonamide and phosphite antioxidants. Moreover, sorbitol derivatives or its by-product may plate out or can be extracted and lead to severe problems especially for food packing products.

2.3.5 Phosphorous-Containing Additives

One of the early players in nucleating agent field was phosphorous containing acid salts like sodium phosphinate. Phosphorous-containing nucleating agents provide greater thermal stability and wider processing windows comparing to sorbitol derivatives.

2.3.6 Organic Acid Derivatives (Later Developments)

Rosin acid based additives have been introduced first by Japanese researchers as efficient organic nucleating agents for PP. Examples of rosin acid based nucleating agents include rosin acid salts and dehydroabietic acid. Other later investigated organic acid nucleating agents are alkaline earth salts including calcium salt, magnesium salt and sodium salt. Among them, sodium salt showed the best nucleation efficiency. These nucleating agents are not only non-toxic with no odor but also are in favor of the low cost of production.
Bicyclo acid based nucleating agents and their derivatives are also highly efficient nucleating agents. Disodium salt of bicyclo [2.2.1] heptane-2,3-dicarboxylic acid commercially launched as Hyperform HPN-68 by Milliken is known to provide a new level of nucleating agent effectiveness for PP. This nucleating agent not only provides common advantages of nucleating agent but also features an excellent balance of impact resistance and stiffness, low incompatibility with other additives and less isotropic shrinkage of material in the mold. This additive showed low hygroscopicity with enhanced life storage. It will not migrate out of the polymer and unlike sorbitol derivatives it does not exhibit problems such as odor or tainting.

Another developed nucleating agent by Milliken is based on salts of hexahydraphthalic acid (cis-1,2-cyclohexane dicarboxylic acid) combined with the acid scavenger like calcium stearate and hydrotalcite. The proposed additive is claimed to be effective for both homo- and co-polymers of PP.

Other proposed organic acid nucleating agents are termed as diamondoid derivatives that are also related to bicyclo acids. Diamondoid derivatives are carboxylic acids or salts thereof based on adamantane or its di-, tri-, tetra-, etc analogous such as 1-adamantane carboxylic acid sodium salt and 1-diadmantabce carboxylic acid.

Recently, the new generation of organic acid nucleating agent based on trisamide of 1,3,5-benzenetricaroxylic acid and analogues compound have been developed by Ciba Specialty Chemicals such as Irgaclear XT386. These series of nucleating agents have generic structure of A – (X-R)₃ which comprises three functional groups including “A” the benzene ring as a central core, “X” the amide and hydrogen bondable part which maximizes surface to
potential ratio through promoting the linear growth of additive crystals and Peripheral R group which is a non-polar substituent. Based on the selected non-polar substituents, crystallographic order of the species as well as the type of crystal formed in the host polymer can be controlled. In fact, the R group enables semi-polar additives dissolution in a polymer melt, especially hydrocarbons. Depending on their chemical structure variation, these additives are capable of selectively yet effectively providing nucleation and growth of monoclinic (α) iPP polymorph as the most favored iPP morphology and making PP films highly transparent at very low concentrations. Others in this group are able to induce hexagonal (β) as a mechanically distinct iPP crystal morphology. Moreover, it is also claimed that special chemical structure of triamide derivatives can induce both α and β crystal forms of iPP. Trisamide derivatives contain amide linkages which are able to build strong hydrogen bonds. In this regard, not only trisamide derivatives are thermally and chemically stable unlike sorbitol derivatives, but also, they can be used as clarifying agent and electret additive. In fact, it is suggested that application of very low concentration of these nucleating agents (0.02 Wt. %) will improve transparency, electrical and charge storage properties of PP. The presence of –NH groups lead to self-assembly and formation of macrodipoles and consequently enhanced charge retention of the host polymer.

2.3.7 β -Nucleators

Certain specific type of nucleating agent can be used to induce the β crystal forms of iPP. β crystalline structure provides more impact strength and higher tear strength of iPP than other polymorphs. The first applied β inducing additive were pigment containing samples, especially quinacridones (e.g., Permanent Red E3B). These additives drawbacks are
bringing color to the final product even at low-level concentrations and providing both α and β polymorphs regarding the thermal history. Other effective β nucleators include calcium pimelate and 2,6-naphthalenedicarboxylic acid dicyclohexamid 
commercially termed as NJ-Star NU-100. It is stated that the amount of induced β-iPP polymorph of NU-100 (85-95%) > Calcium pimelate (60-90%) > quinacridone (60-70%).

2.3.8 Nanoparticles

Nanoparticles seem to be able to provide very small nucleating sites and deliver much higher nucleation efficiency than the other available nucleating agents. However, for nanoparticles to be accounted as efficient nucleating agents two important criteria should be fulfilled. Firstly, the applied particles sizes should meet the limit suggested by the surface of the crystal lattice. In the case of iPP, the estimated limit falls between 20 and 40 nm. Secondly, nanoparticles should be well dispersed in the host polymer which is a very critical criteria. Different types of nanofillers that can be applied for PP include organoclays (organically intercalated montmorillonite, OMMT), carbon nanotubes (CNT, single-walled (SWNT) and multi-walled (MWNT)), precipitated calcium carbonate (PCC) and etc. Among these nanofillers, organoclay is the most used one. Based on DSC analysis at the cooling rate of 10 K/min, it is suggested that presence of 3 wt. % of modified organoclay increased the onset crystallization temperature (T_c) from 111 to 115 °C. Considering the fact that application of mineral talc leads to better nucleation effects, so the nucleating effect of organoclay can be doubted. In the case of carbon nanotubes, small nucleation effect was observed in crystallization from the quiescent melt. According to DSC analysis of SWNT containing PP sample, onset crystallization temperature increased by 6 °C, at a cooling rate of 10 °C/min.
On the other hand, application of MWNT for PP fiber led to mechanical reinforcement and decreased crystallinity comparing to the pure PP fiber. Based on those results, it was concluded that passive particles might just affect flow-induced crystallization. Otherwise, better mechanical properties can be attributed to “shish kebob” structure which might be fashioned for PP fibers. Calcium carbonate and precipitated calcium carbonate (PCC) showed limited nucleating activity and with the addition of over 10 wt. % concentration of these particles only 10 °C increase of Tc was observed. Also according to another study, with addition of up to 3 wt. % concentration of nanoclay for developing melt-spun PP fibers, onset crystallization temperature of polymer increased while crystallinity of fibers did not changed significantly.

2.3.9 Miscellaneous

Over 50 years or so various types of nucleating agents have been developed other than the ones mentioned in pervious sections but very few of them were commercialized such as polypropylene- 1, 3- diketone metal salts and diphenylglycines, isotactic polystyrene-melamine, salicylamide, cyanuric acid, uracil deravitives, azodicarboxylic amides, stearamide, saccharin, nicotinamide, zinc glycerolate, steramide with HDPE, mono-or diurea derivatives and etc.

2.4 Nucleating Agents as Electret Additives

Polymers electret properties privileged several high-tech required inventions including aerosol filters, electret ion chambers, microphones and radiation sensors. Most studies were focused on improving the electret properties of films. Recently, research has been conducted
to study the effect of electret additives on polarization properties of polymers and electret properties of the fiber-based devices. Electret filter is an example of fiber-based devices which found technical and commercial interest lately. Electret additives are able to not only enhance charge density but also charge stability of the electret filters. Electret filter is an example of fiber-based devices which found technical and commercial interest lately. Electret filters filtration efficiency is highly dominated by the electret field strength of the fibrous media. In this regard, charge stability is very important since high initial charge density does not guarantee high charge stability. In fact, loss of charge can lead to significant decrease of filter media total filtration performance. Additives can be used to improve both charge density and stability, however, there is no specific additive designed specifically for this purpose. In this regard, nucleating agents, light stabilizers, fluorochemicals, inorganic additives, and antioxidants can be used to improve charge retention and stability. In the case of filters, loss of charge can be attributed to the creation of conductive film upon filtration.

Fluorochemicals have been used to prevent conductive film formation and charge decay. According to recent investigations, application of BaTiO$_3$ as an additive with high dielectric constant in PP meltblown nonwovens led to improved charging and filtration properties of the developed PP electret nonwoven filters. Moreover, charge retention and stability of the studied electret filters was promising. Also, morphology of the fibers did not changed significantly with addition of BaTiO$_3$. Uniformly and thermally charged samples showed superior stable electret filtration properties. Accelerated decay test was applied for PP nonwoven filters containing over 1% BaTiO$_3$. Results showed filtration efficiency as well
as charge stability of filters increased significantly upon application of BaTiO$_3$. Moreover, filtration performance of nonwoven filters containing over 1% BaTiO$_3$ did not alter significantly after isothermal decay test.$^{79}$

Beside dielectric additives, nucleating agents also can be applied to improve electret properties of films.$^{50,62,63,73,83–86}$ Nucleating agents showed potential to enhance electret properties of polymeric products$^{62,63,73,83}$. Application of nucleating agents leads to the formation of small spherulites whose boundaries act as traps for space charges. Moreover, microvoids can be generated upon addition of nucleating agents which prohibits charge migration$^{62}$. Unlike some other additives, nucleating agents can be buried into crystallites where charge stability is better than the amorphous regions$^{74}$. Different types of nucleating agents such as trisamide and its derivatives$^{62,63}$, sodium 2,2′– methylene bis (4,6-di-terbutylphenyl)-phosphate (NA11)$^{73,84}$, bisamide$^{84}$, N,N′–dicyclo-haxyl-2,6-naphthalene-dicarbox-amide (NU100)$^{85}$ and etc. have been examined as electret additives.

Effect of 1,4-phenylene bisamides as crystal nucleators on chargeability of PP film was investigated. Nucleation ability as well as PP film charge stability was disturbed in the presence of bisamides containing long aliphatic side chains. Symmetry and concentration of additives play important roles on electret properties of the final products$^{67}$. However, concentration showed more impact on charge stability. It is suggested that, application of below 0.05 wt. % concentration of bisamide additives for PP films resulted in 20% increase of charge stability compared to the remained potential after annealing for 24 h at 90 ◦C$^{86}$. At higher concentrations of nucleating agent, not only the network will be formed but also aggregation of insoluble additive happens because of percolation$^{86}$. 

41
Similarly, application of 0.04 wt. % (high concentration) triphenylamine based trisamides provides sufficient quantities of charge carriers to provide high conductivity\textsuperscript{62}. Presence of –NH groups in amide containing trisamides lead to self-assembly and formation of macrodipoles and consequently enhanced charge retention of the host polymer. Trisamides without amide groups showed worst stability than the pure films. In fact, percolation can happen at higher concentrations where larger 3D network structure is fashioned\textsuperscript{63}.

On the other hand, application of nucleating agents like NA11 that does not dissolve in PP may lead to the formation of micro-voids during the film manufacturing process\textsuperscript{73,84}. In this case, electret properties depend on the fashioned elongated voids which are considered as potential charge barriers against decay. Polymeric films containing NA11 charge stability will be improved upon stretching due to formation of more cavities\textsuperscript{73,84}. It was observed that, in the case of application of below 0.5 wt. % concentration of NU100, charge decay was faster comparing to the pure iPP\textsuperscript{74}. This happens due to the formation of 3D network structure pathways for charge carriers provided by hydrogen bonds\textsuperscript{74}. Antioxidants can be applied as nucleating agents and render deep charge traps\textsuperscript{87}.

Effect of commercially available nucleating agents including NA11 and DMDBS was studied on PP fibers and nonwovens filtration and charging properties\textsuperscript{75,74}. In case of nonwovens containing these nucleating agents, samples were charged at both room and elevated temperatures to investigate the effect of nucleating agents on charging properties of PP nonwovens\textsuperscript{74}. Thermally charged webs containing nucleating agents provided not only enhanced electrostatic potential but also improved filtration properties. These improvements are attributed to higher potential values originated from dielectric properties of the mentioned
nucleating agents. This is the reason that additives with high polarizability are suitable candidates for improving both charge density and stability of materials. In the case of addition of those mentioned nucleating agents for fibers, NA11 showed more impact on charge stability while DMDBS containing samples showed more decay. However, upon charging at elevated temperature of samples contained NA11 and DMDBS, charge density and stability improved. But, cold charging was not effective. Polarization of these additives molecule is the main reason behind enhanced charge density and stability of the developed materials.

2.5 Nucleating Agents Application in Crystallization from Quiescent Polymer Melt, Melt Spinning and Meltblowing Processes

Application of nucleating agents for crystallization from quiescent polymer melt results in higher degree of crystallinity and onset crystallization temperature of polymers, higher thermal stability, improved electret, optical and physical properties of the produced materials like polymeric films. Also, with addition of nucleating agent in melt spinning process, crystallization rate and temperature of polymers will be increased. In the melt spinning process, crystallization is not only governed by super cooling but also by stress. At higher spinline stress, rate of crystallization is very high and effect of nucleating agent would not be very impressive, although it is not completely eliminated. In this regard, nucleating agent influence might be more pronounced at low spinning speeds. According to different studies, the applied stress for melt-spinning of PET fibers is 3-4 orders of magnitude larger comparing to the quiescent conditions.
Therefore, it is expected that in the highly oriented PET crystalline structure, crystallization can occur very rapid \(^{20}\). However, there is always a competition between relaxation and crystallization. At low extension rates the volume element chains relaxation happens and crystallization will not occur. But at higher spinning speeds, little relaxation takes place before the occurrence of crystallization or frizzed oriented amorphous phase formation \(^{20}\). In practice, high spinning speed is required not only to outstrip the relaxation but also to achieve some degree of crystallinity before reaching the glass transition temperature \(^{20}\). For PET as a slow crystallizing polymer and Nylon 6, crystallization during spinning is not possible unless the critical take-up velocity of 3000-4000 m/min is reached \(^{20}\). In these high spinning speeds, impact of nucleating agent on crystallization would not be very impressive since crystallization happens very quick \(^{26}\). Online spinline crystallization studies at low take up speeds have been performed on polymers including polypropylene, nylon 6, PET, poly (vinylidene fluoride), polybutene-1, nylon 66 and poly (ethylene naphtalate) \(^{20}\). Results suggested that crystallization in the spinline is more likely to happen at high spinning speeds which are related to the formation of the neck in fibers and other effects associated with high spinning speeds. At low spinning speeds, since the driving force is not large enough, the developed fiber has intermediate orientation with no or very low degree of crystallinity. In this case, crystallization probably can be influenced by nucleating agents \(^{25, 26}\). With addition of nucleating agent, crystallization tends to occur at a higher temperature closer to the spinneret, where the molecular orientation is lower in the melt so lower orientation for the product is expected \(^{26}\). In this regard, due to reduction of molecular orientation decrease of modulus is quite possible, even though higher degree of crystallinity can be obtained in
presence of nucleating agent. Reduction of orientation in presence of nucleating agent may lead to higher elongation of the developed fibers. Nucleating agent is reported to be effective in increasing the porosity as well as water flux of PP fiber membrane made through melt spinning process. Also according to another study, with addition of up to 3 wt. % concentration of nanoclay for developing melt spun PP fibers, onset crystallization temperature of polymer increased while crystallinity % of fibers did not changed significantly. Application of nucleating agent for nylon 66 fibers led to decrease of induction time and higher rate of crystallization while it did not show significant impact on crystallinity of fibers.

For meltblowing process, application of nucleating agent may lead to faster solidification of polymer melt, lower solidity and higher air permeability of webs. Moreover, nucleating agent can impact electret properties of the developed nonwovens. Effect of commercially available nucleating agents including NA11 and DMDBS was studied on PP fibers and nonwovens filtration and charging properties. In the case of nonwovens containing the noticed nucleating agents, solidity of webs decreased while air permeability of them increased. Moreover, samples were charged at both room and elevated temperatures to investigate the effect of nucleating agents on charging properties of PP nonwovens. Thermally charged webs containing nucleating agents, provided not only enhanced electrostatic potential but also improved filtration properties. These improvements are attributed to higher potential values originated from dielectric properties of NA11 and DMDBS nucleating agents. This is the reason that additives with high polarizability are suitable candidates for improving both charge density and stability of materials. In the case
of addition of those mentioned nucleating agents for fibers, NA11 showed more impact on charge stability while samples containing DMDBS showed more decay. However, upon charging at elevated temperature of samples containing NA11 and DMDBS, charge density and stability improved. But, cold charging was not effective. Polarization of these additives molecule is the main reason behind enhanced charge density and stability of developed materials.
2.6 References


29. Randall R. Bresee & Wen-Chien Ko. Fiber Formation During Melt Blowing. 12, 21–28


50


51. Bernland, K., Tervoort, T. & Smith, P. Phase behavior and optical- and mechanical properties of the binary system isotactic polypropylene and the nucleating/clarifying agent 1,2,3-trideoxy-4,6:5,7-bis-O-[(4-propylphenyl) methylene]-nonitol. Polymer 50, 2460–2464 (2009).


58. Jiong Yu, Tad Finnegan and Ralph Maier. Available at:


75. Kilic, A., Shim, E., Yeom, B. Y. & Pourdeyhimi, B. Effect of DMDBS (3 : 2, 4-bis(3,4-
dimethyldibenzylidene) sorbitol) and NA11 (sodium 2,2’-methylene-bis(4,6-di-
tertbutylphenyl)-phosphate) on electret properties of polypropylene filaments. J. Appl.


77. Eitzman, P. D. & Rousseau, A. D. Method and apparatus for making a fibrous electret
web using a wetting liquid and an aqueous polar liquid. (2002).

78. Rousseau, A. D., Jones, M. E. & Angadjivand, S. A. Fibrous webs having enhanced
electret properties. (1999).

79. Kilic, A., Shim, E. & Pourdeyhimi, B. Electrostatic Capture Efficiency Enhancement of
Polypropylene Electret Filters with Barium Titanate. Aerosol Sci. Technol. 49, 666–673

80. Rousseau, A. D., Jones, M. E. & Mei, B. Z. Electret articles and filters with increased

81. Rousseau, A. D., Jones, M. E. & Mei, B. Z. Method of making electret articles and filters
with increased oily mist resistance. (2000).


83. Behrendt, N., Altstadt, V., Schmidt, H. W., Zhang, X. & Sessler, G. M. Development of
porous polypropylene blends with NA11 particles and glass hollow spheres by biaxial


3. **Effect of 1,3,5-tris(2,2-dimethylpropionylamino)benzene (Irgaclear XT 386) on Crystallization and Crystalline Structure of Polypropylene Films**

3.1 **Abstract**

Polypropylene films with different concentration of 1,3,5-tris(2,2-dimethylpropionylamino)benzene (commercially known as Irgaclear XT 386) nucleating agent were produced through Brabander film extrusion process. The effect of this nucleating agent on crystallization behavior and crystalline structure of the produced polypropylene (PP) films was investigated. Results indicate utilization of Irgaclear XT 386 leads to higher onset crystallization temperature of polymer, increased crystallinity % and the alteration in crystalline structure of PP films.

**Key words:** Polypropylene films, nucleating agent, Irgaclear XT 386, crystallization, crystalline structure.

3.2 **Introduction**

Crystallization is a physical transition of material from disordered structure in liquid phase to ordered one in solid state \(^1\), \(^2\). Physical, thermal, chemical and optical properties of the developed polymeric products are highly influenced by the crystallization process \(^3\). Due to chain connectivity, only limited crystallinity could be obtained through polymer crystallization \(^4\). Nucleating additives, are considered to be able to facilitate crystallization process and change the properties and functionalities of polymers \(^5\).
In the case of crystallization from quiescent polymer melt, upon slowly cooling the polymer melt below its melting temperature, crystallization happens via nucleation and crystal growth. Lamella as a secondary crystal structure will be fashioned consequently. Further crystal growth leads to the formation of ribbon-like strips from larger lamellae. Upon branching, twisting, stacking and folding together, ribbon-like strips are able to form larger size (tens of microns) tertiary structures called spherulites. Enveloping the entire volume, spheres of growing crystals meet each other and straight or curved boundaries will be formed. In this case application of nucleating agents can lead to formation of smaller size spherulites, higher degree of crystallinity and onset crystallization temperature, reduced process cycle time, improved electret, optical and physical properties of the developed materials.

Nucleating agents can be applied for polymers which crystal growth rate is neither too high nor too low. Due to its commercial advantages and its moderate crystal growth rate, PP is the most commonly used polymer to investigate the effect of the nucleating agent on polymers. Nucleating agents regarding their chemical structures can be classified into two different categories including organic nucleating agents such as organophosphate, trisamide and sorbitol derivatives and inorganic ones like calcium carbonate, talc and magnesium hydroxide. Recently, the new generation of organic acid nucleating agent based on trisamide of 1,3,5-benzenetricarboxylic acid and analogues compound have been developed by Ciba Specialty Chemicals such as 1,3,5-tris(2,2-dimethylpropionylamino)benzene commercially known as Irgaclear XT386. These series of nucleating agents have generic structure of \( A - (X-R)_3 \) which comprises three functional groups including “A” the benzene ring as a central
core, “X” the amide and hydrogen bondable part which maximizes surface to potential ratio through promoting the linear growth of additive crystals and peripheral R group which is a non-polar substituent. Based on the selected non-polar substituents, crystallographic order of the species as well as type of crystal formed in the host polymer can be controlled. In fact, the R group enables semi-polar additives dissolution in a polymer melt, especially hydrocarbons. Depending on their chemical structure variation, these additives are capable of selectively yet effectively providing nucleation and growth of monoclinic (α) iPP polymorph as the most favored iPP morphology and making PP plastics highly transparent at very low concentrations. Others in this group are able to induce hexagonal (β) as a mechanically distinct iPP crystal morphology. Moreover, it is also claimed that special chemical structure of triamide derivatives can induce both α and β crystal forms of iPP.

1,3,5-tris(2,2-dimethylpropionylamino)benzene (commercially known as Irgaclear XT 386) nucleating agent used in this study contains amide linkages which are able to build strong hydrogen bonds. Therefore, it is claimed that, they are thermally and chemically stable in different environments unlike sorbitol derivatives. Moreover, presence of –NH groups in Irgaclear XT 386 chemical structure can lead to self-assembly and formation of macro dipoles and consequently enhanced charge retention of the host polymer. By application of small amount (~100-200 ppm) of the noticed melt sensitive trisamide derivative, a finely distributed crystalline domain will be formed upon cooling which provides a huge nucleation surface for the crystallization process. In this study, to investigate the effect of nucleating agent on crystallization and crystalline structure of PP films, a commercially available nucleating agent, Irgaclear XT 386 is used to develop PP films.
3.3 Materials and Methods

3.3.1 Materials
Spunbond-grade PP (PP CP360H, melting index = 35 g/10min) used in this study was provided by Braskem. The 1,3,5-tris(2,2-dimethylpropionylamino)benzene nucleating agent commercially known as Irgaclear XT386 was kindly supplied by BASF.

3.3.2 Production of PP Film with Nucleating Agent
Production of PP films with nucleating agent was accomplished through two steps. First, nucleating agent and polymer was melt pre-compounded to produce PP/nucleating agent master batch with 10 wt. % concentration of nucleating agent. In the next step, PP were mixed with different amount of the PP/nucleating agent masterbatch and melt extruded through the Brabender film extrusion line to produce films with nucleating agent concentration of 0 (control), 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 wt. %. The melt throughput and the die temperature were 7 g hole\(^{-1}\) min\(^{-1}\) and 210 °C, respectively.

3.3.3 Differential Scanning Calorimetry Analysis
Crystallization and melting characteristics of PP films containing nucleating agent were studied using a TA Discovery differential scanning calorimeter under nitrogen atmosphere. Samples with average weight of 5-10 mg were heated from 25 °C to 195°C and kept at 195°C for 5 min to remove their pervious thermal history. Then they were cooled from 195°C to 25 °C. For all these steps the heating and cooling rates were fixed on 10 °C/min.
Crystallinity % of fibers was determined with the following equation:

\[
\text{Crystallinity} \, (\%) = \frac{\Delta H}{\Delta H^0} \times 100 \tag{1}
\]

Where \(\Delta H\) stands for enthalpy of fusion for fibers (J/ g) and \(\Delta H^0\) is defined as enthalpy of fusion for 100% crystalline PP polymer (207 J/g)\(^1\).

### 3.3.4 Wide-angle X-ray Diffraction Analysis (WAXD)

To evaluate the crystalline structure and crystal size of the samples, Wide-angle X-ray Diffraction (WAXD) tests were carried out with an Omni Instrumental Wide Angle X-Ray Diffractometer using the be-filtered Cu K\(\alpha\) radiation with a wavelength of 1.54 Å. The WAXD spectra were obtained at a voltage of 35 kV and 25 mA current. Samples were scanned in 2θ range of 5-40 (0.05 increments). Crystal size can be determined from scattering pattern according to Scherer’s equation\(^16\):

\[
t = \frac{0.9 \times \lambda}{B \times \cos \theta_B} \tag{2}
\]

where \(t\) represents the crystal size (Å), \(B\) is the full width at half- maximum (rad), \(\lambda\) is the wavelength of X-ray (1.54 Å) and \(\theta_B\) is the Bragg angle.

### 3.4 Result and Discussion

#### 3.4.1 Differential Scanning Calorimetry Analysis

**DSC Cooling Thermogram**

Thermal transition temperature for cooling thermogram of crystallization is highly influenced by presence of nucleating agent in the polymer (see figure 3.1). According to crystallization
graph, as the Irgaclear XT 386 concentration increases to 0.01 wt. %, onset crystallization temperature of polymer increased to 132 °C and peak of crystallization shifted to right.

**Figure 3.1**: DSC cooling thermogram of PP films containing different concentration of Irgaclear XT 386 (crystallization exotherm)

By further increasing the amount of nucleating agent, onset crystallization temperature of polymer did not changed. Onset crystallization temperatures of all samples are given in table 3.1. In fact, due to presence of nucleating agent there would be more nuclei in polymer melt and supersaturation happens from the very early stage of cooling process. Therefore, for samples containing Irgaclear XT 386 more crystals can be fashioned comparing to PP control sample and crystallization will start at higher temperature.
Table 3.1: Onset crystallization temperature for PP films containing Irgaclear XT 386

<table>
<thead>
<tr>
<th>Nucleating agent conc. wt. %</th>
<th>Onset Crystallization Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>121</td>
</tr>
<tr>
<td>0.01</td>
<td>132</td>
</tr>
<tr>
<td>0.02</td>
<td>132</td>
</tr>
<tr>
<td>0.03</td>
<td>132</td>
</tr>
<tr>
<td>0.04</td>
<td>132</td>
</tr>
<tr>
<td>0.05</td>
<td>132</td>
</tr>
<tr>
<td>0.1</td>
<td>132</td>
</tr>
<tr>
<td>0.2</td>
<td>132</td>
</tr>
<tr>
<td>0.3</td>
<td>132</td>
</tr>
<tr>
<td>0.4</td>
<td>132</td>
</tr>
<tr>
<td>0.5</td>
<td>132</td>
</tr>
</tbody>
</table>

DSC Heating Thermogram

According to DSC heating thermograms of fibers shown in figure 3.2, by application of nucleating agent shape of melting peaks did not change significantly. As can be seen in table 3.2, the onset melting temperature of samples slightly increased from 155 °C for PP control sample to 157 °C for sample with 0.5 wt. % concentration of nucleating agent. The increase of onset melting temperature can be due to formation larger crystals for samples with 0.5 wt. % concentration of nucleating agent.
Figure 3.2: DSC heating thermogram of PP films containing different concentration of Irgaclear XT386 (melting endotherm)

Overall crystallinity is calculated from the total area of heating thermogram of the melting endotherm. As can be seen in figure 3.3, crystallinity % increased from 44 to 48 as the nucleating agent concentration increased to 0.4 wt. %. This is because of the changes in crystallization process in presence of nucleating agent. However, by increasing the amount of nucleating agent to 0.5 wt. % of Irgaclear XT 386, crystallinity
% decreased. The reason behind this phenomenon could be utilization of too much additive that leads to agglomeration and formation of larger crystals sizes 2.

Table 3.2: DSC heating thermograms analysis of PP films containing different concentration of Iragclear XT 386

<table>
<thead>
<tr>
<th>Nucleating agent conc. wt. %</th>
<th>Onset Melting Temperature (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>155</td>
<td>44</td>
</tr>
<tr>
<td>0.01</td>
<td>156</td>
<td>47</td>
</tr>
<tr>
<td>0.02</td>
<td>156</td>
<td>48</td>
</tr>
<tr>
<td>0.03</td>
<td>156</td>
<td>48</td>
</tr>
<tr>
<td>0.04</td>
<td>156</td>
<td>48</td>
</tr>
<tr>
<td>0.05</td>
<td>157</td>
<td>48</td>
</tr>
<tr>
<td>0.1</td>
<td>157</td>
<td>48</td>
</tr>
<tr>
<td>0.2</td>
<td>157</td>
<td>48</td>
</tr>
<tr>
<td>0.3</td>
<td>157</td>
<td>48</td>
</tr>
<tr>
<td>0.4</td>
<td>157</td>
<td>48</td>
</tr>
<tr>
<td>0.5</td>
<td>157</td>
<td>46</td>
</tr>
</tbody>
</table>
3.4.2 Crystalline structure

Polymeric film crystalline morphology changes can be monitored via WAXD. WAXD patterns of PP films and PP films containing nucleating agent are shown in figure 3.4. According to the X-ray diffractogram of PP film, the crystalline peaks are broad and occur at a 2θ value of 14.5255, 17.8676, 19.7144 and 22.6505 which are correspondent to α crystalline form of isotactic PP \(^\text{17}\). However, for samples containing Irgaclear XT 386, the crystalline peaks are sharper and more distinct which suggests formation of well-shaped crystals in presence of nucleating agents.
The crystal size, the Bragg angle as well as the Full Width at Half Maximum (FWHM) for each individual peak are listed in table 3.3. According to this table for PP film containing 0.01 wt. % conc. of nucleating agent crystals sizes decreased compared to the control PP film. However, as the concentration of nucleating agent increased to 0.5 wt. % crystals sizes increased compared to film containing 0.01 wt. % concentration of nucleating agent, although they remained smaller compared to PP control film crystals sizes. Formation of larger crystal size for PP films with 0.5 wt. % concentration of nucleating agent can be due to utilization of too much additive that might lead to additive agglomeration.

**Figure 3.4**: X-ray diffractogram of PP films containing different concentration of Irgaclear XT 386
**Table 3.3**: Crystalline size of PP films containing different concentration of Irgaclear XT 386

<table>
<thead>
<tr>
<th>Nucleating agent conc. (wt. %)</th>
<th>Angle (2θ)</th>
<th>FWHM (radian)</th>
<th>Crystal size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.5</td>
<td>0.017</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>17.8</td>
<td>0.004</td>
<td>296</td>
</tr>
<tr>
<td></td>
<td>19.7</td>
<td>0.002</td>
<td>553</td>
</tr>
<tr>
<td></td>
<td>22.6</td>
<td>0.012</td>
<td>118</td>
</tr>
<tr>
<td>0.01</td>
<td>14.5</td>
<td>0.020</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>17.3</td>
<td>0.016</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>19.2</td>
<td>0.009</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>21.9</td>
<td>0.024</td>
<td>57</td>
</tr>
<tr>
<td>0.02</td>
<td>14.1</td>
<td>0.012</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>16.8</td>
<td>0.011</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>0.012</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>0.011</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>21.7</td>
<td>0.015</td>
<td>91</td>
</tr>
<tr>
<td>0.03</td>
<td>14.8</td>
<td>0.014</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>17.6</td>
<td>0.011</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>19.4</td>
<td>0.013</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>21.9</td>
<td>0.013</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>22.7</td>
<td>0.013</td>
<td>106</td>
</tr>
<tr>
<td>0.04</td>
<td>14.1</td>
<td>0.012</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>16.8</td>
<td>0.010</td>
<td>134</td>
</tr>
<tr>
<td></td>
<td>18.6</td>
<td>0.012</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td>21.1</td>
<td>0.010</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td>21.9</td>
<td>0.013</td>
<td>108</td>
</tr>
<tr>
<td>0.05</td>
<td>13.9</td>
<td>0.009</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>0.007</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>18.4</td>
<td>0.006</td>
<td>221</td>
</tr>
<tr>
<td></td>
<td>20.9</td>
<td>0.007</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>21.7</td>
<td>0.011</td>
<td>127</td>
</tr>
</tbody>
</table>
Table 3.3: Continued

<table>
<thead>
<tr>
<th>Nucleating agent conc. (wt. %)</th>
<th>Angle (2θ)</th>
<th>FWHM (radian)</th>
<th>Crystal size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>14.2</td>
<td>0.010</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>0.008</td>
<td>168</td>
</tr>
<tr>
<td></td>
<td>18.7</td>
<td>0.007</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>21.3</td>
<td>0.007</td>
<td>192</td>
</tr>
<tr>
<td></td>
<td>22.9</td>
<td>0.009</td>
<td>150</td>
</tr>
<tr>
<td>0.2</td>
<td>14.1</td>
<td>0.011</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>16.8</td>
<td>0.008</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>18.6</td>
<td>0.009</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>21.1</td>
<td>0.008</td>
<td>168</td>
</tr>
<tr>
<td></td>
<td>21.9</td>
<td>0.012</td>
<td>114</td>
</tr>
<tr>
<td>0.3</td>
<td>14.2</td>
<td>0.014</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>16.9</td>
<td>0.012</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>18.8</td>
<td>0.016</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>21.2</td>
<td>0.010</td>
<td>134</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>0.015</td>
<td>89</td>
</tr>
<tr>
<td>0.4</td>
<td>14.2</td>
<td>0.012</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>16.9</td>
<td>0.009</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>18.7</td>
<td>0.008</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>21.2</td>
<td>0.005</td>
<td>236</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>0.011</td>
<td>119</td>
</tr>
<tr>
<td>0.5</td>
<td>14.1</td>
<td>0.013</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>16.9</td>
<td>0.011</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>18.6</td>
<td>0.014</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>21.1</td>
<td>0.012</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>21.9</td>
<td>0.015</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>25.4</td>
<td>0.011</td>
<td>120</td>
</tr>
</tbody>
</table>

3.5 Conclusion

The effect of Irgaclear XT 386 nucleating agent on crystallization and crystalline structure of PP films has been investigated. Results showed that, by application of Irgaclear XT 386, onset crystallization temperature of polymer increased from 121 ºC for PP control film to 132
°C for PP films containing nucleating agent. Moreover, crystallinity % of samples slightly increased as the Irgaclear XT 386 concentration increased to 0.4 wt.%, while at higher concentration of nucleating agent, crystallinity % decreased. WAXD analysis indicated that, for samples containing 0.01 wt. % concentration of Irgaclear XT 386 crystals sizes decreased. However, for samples with higher concentration of nucleating agent (0.02-0.5 wt. %) crystals sizes increased compared to film containing 0.01 wt.% concentration of nucleating agent, although they remained smaller compared to PP control film crystals sizes.
3.6 References


11. Fairgrieve, S. *Nucleating Agents.* (Smithers Rapra, 2005).


4. The Effect of 1,3,5-tris(2,2-dimethylpropionylamino)benzene (Irgaclear XT 386) on Crystalline Structure and Properties of Meltspun Polypropylene Fibers

4.1 Abstract

Meltspun polypropylene fibers with different concentration of nucleating agent 1,3,5-tris(2,2-dimethylpropionylamino)benzene (commercially known as Irgaclear XT 386) were produced by melt-spinnning process. The effect of this nucleating agent on crystallization behavior, crystalline structure and mechanical properties of the produced meltspun polypropylene (PP) fibers was investigated. Results indicate utilization of Irgaclear XT 386 leads to higher onset crystallization temperature of polymer, a slight change in degree of crystallinity and the alteration of crystalline structure of PP meltspun fibers. According to tensile testing analysis, with addition of the so-called nucleating agent, the single fiber elongation and toughness increased while tenacity decreased.

Keywords: Polypropylene fiber, nucleating agent, crystallization, crystalline structure, mechanical properties

4.2 Introduction

Crystallization is a physical transition of material from disordered structure in liquid phase to ordered one in solid state. Mechanical, thermal, chemical and optical properties of the developed polymeric products are highly influenced by the crystallization process.
Due to chain connectivity, only limited crystallinity could be obtained through polymer crystallization. Nucleating agents, are considered to be able to facilitate crystallization process and change crystalline structures of polymeric materials.

In the case of crystallization from quiescent polymer melt, upon slowly cooling the polymer melt below its melting temperature, crystallization happens via nucleation and crystal growth. Lamella as a secondary crystal structure will be fashioned consequently. Further crystal growth leads to the formation of ribbon-like strips from larger lamellae. Upon branching, twisting, stacking and folding together, ribbon-like strips are able to form larger size (tens of microns) tertiary structures called spherulites. Enveloping the entire volume, spheres of growing crystals met each other and straight or curved boundaries will be formed.

In this case application of nucleating agents can lead to formation of smaller size spherulites, higher degree of crystallinity and onset crystallization temperature, reduced process cycle time, improved electret, optical and physical properties of the materials.

Nucleating agents can be applied for polymers which crystal growth rate is neither too high nor too low. Due to its commercial advantages and its moderate crystal growth rate, PP is the most commonly used polymer to investigate the effect of the nucleating agent on polymers. Nucleating agents regarding their chemical structures can be classified into two different categories including organic nucleating agents such as organophosphate, trisamide and sorbitol derivatives and inorganic ones like calcium carbonate, talc and magnesium hydroxide. Recently, the new generation of organic acid nucleating agent based on trisamide of 1,3,5-benzenetricarboxylic acid and analogues compound have been developed by Ciba Specialty Chemicals such as Irgaclear XT386. These series of nucleating agents have
generic structure of A – (X-R)_3 which comprises three functional groups including “A” the benzene ring as a central core, “X” the amide and hydrogen bondable part which maximizes surface to potential ratio through promoting the linear growth of additive crystals and peripheral R group which is a non-polar substituent. Based on the selected non-polar substituents, crystallographic order of the species as well as type of crystal formed in the host polymer can be controlled. In fact, the R group enables semi-polar additives dissolution in a polymer melt, especially hydrocarbons. Depending on their chemical structure variation, these additives are capable of selectively yet effectively providing nucleation and growth of monoclinic (α) iPP polymorph as the most favored iPP morphology and making PP films highly transparent at very low concentrations. Others in this group are able to induce hexagonal (β) as a mechanically distinct iPP crystal morphology. Moreover, it is also claimed that special chemical structure of triamide derivatives can induce both α and β crystal forms of iPP.

The trisamide derivative 1,3,5-tris(2,2-dimethylpropionylamino)benzene, commercially known as Irgaclear XT 386 used in this study contains amide linkages which are able to build strong hydrogen bonds. Therefore, it is claimed that, they are thermally and chemically stable in different environments unlike sorbitol derivatives. Moreover, the presence of –NH groups in Irgaclear XT 386 chemical structure can lead to self-assembly and formation of macrodipoles and consequently enhanced charge retention of the host polymer. By application of small amount (150-200 ppm) of the noticed melt sensitive trisamide derivative, a finely distributed crystalline domain will be formed upon cooling which provides a huge nucleation surface for the crystallization process. In this regard, utilization of very low
concentration of Irgaclear XT 386 can lead to, decreased spherulite size, higher rate of crystallization and degree of crystallinity, higher thermal stability, improved electret, optical and mechanical properties of the developed polymeric materials like films

In the melt-spinning process, crystallization plays an important role in developing final products. Fibers are developed under extreme molecular orientation and driving forces. The presence of crystals in semicrystalline synthetic fiber structure is necessary to avoid shrinkage under different conditions (e.g. cleaning) and to provide required strength and stiffness. In meltspinning process the first step of crystallization as an ordering of the polymer chains in a side-by-side structure is similar for both crystallization from a quiescent melt and crystallization during a mechanical deformation. But when it comes to higher order structures, crystallization shares few characteristics with spherulites. In this regard, at least, two common morphologies including shish-kebab and microfibrils structures are expected. So, the morphology and crystalline structure of textiles fashioned upon crystallization under the stress is different from that of the crystallization from quiescent polymer melt. In this regard, the effect of nucleating agent on the morphology and mechanical properties of materials developed under either of those conditions is anticipated to be different. In melt spinning process, the crystallization is governed not only by super cooling but also by stress. At higher spinline stress, rate of crystallization is very high and effect of nucleating agent would not be very impressive, although it is not completely eliminated. In this regard, nucleating agent influence might be more pronounced at low spinning speeds. According to different studies, the applied stress for melt-spinning of PET fibers is 3-4 orders of magnitude larger comparing to the quiescent conditions. Therefore, it is expected that in the
highly oriented PET crystalline structure, crystallization can occur very rapid. However, there is always a competition between relaxation and crystallization. At low extension rates the volume element chains relaxation happens and crystallization will not occur. But at higher spinning speeds, little relaxation takes place before the occurrence of crystallization or frizzed oriented amorphous phase. In practice, high spinning speed is required not only to outstrip the relaxation but also to achieve some degree of crystallinity before reaching the glass transition temperature. For PET as a slow crystallizing polymer and Nylon 6, crystallization during spinning is not possible unless the critical take-up velocity of 3000-4000 m/min is reached. In these high spinning speeds, impact of nucleating agent on crystallization would not be very impressive since crystallization happens very quick.

Online spinline crystallization studies at low take up speeds have been performed on polymers including polypropylene, nylon 6, PET, poly (vinylidene fluoride), polybutene-1, nylon 66 and poly (ethylene naphtalate). Results suggested that crystallization in the spinline is more likely to happen at high spinning speeds which are related to the formation of the neck in fibers and other effects associated with high spinning speeds. At low spinning speeds, since the driving force is not large enough, the developed fiber has intermediate orientation with no or very low degree of crystallinity. In this case, crystallization probably can be influenced by nucleating agents. With addition of nucleating agent, crystallization tends to occur at a higher temperature closer to the spinneret, where the molecular orientation is lower in the melt so lower orientation for the product is expected. In this regard, decrease of modulus is quite possible due to reduction of molecular orientation, even though higher degree of crystallinity can be obtained in presence of nucleating agent. Reduction of
orientation in presence of nucleating agent may lead to higher elongation of the developed fibers. Nucleating agent is reported to be effective in increasing the porosity as well as water flux of PP fiber membrane made through melt spinning process \(^{24}\). Also according to another study, with addition of up to 3 wt. % concentration of nanoclay for developing melt spun PP fibers, onset crystallization temperature of polymer increased while crystallinity of fibers did not changed significantly. Application of nucleating agent for nylon 66 fibers led to decrease of induction time and higher rate of crystallization while it did not show impact on crystallinity of fibers \(^{25}\).

In fact, the effect of nucleating agent on fibers is not a completely understood phenomenon which provides plenty of room for research and innovation. So, it is of interest to explore if similar properties obtained for films by application of nucleating agents can be translated in fibers as well. In this study, to investigate the effect of nucleating agent on morphology and mechanical properties of meltspun fibers, a commercial nucleating agent, Irgaclear XT 386 is used to develop PP fibers.

**4.3 Materials and Methods**

**4.3.1 Materials**

Spunbond-grade PP (PP CP360H, melting index = 35 g/10min) used in this study was provided by Braskem. The 1,3,5-tris(2,2-dimethylpropionylamino)benzene nucleating agent commercially known as Irgaclear XT386 was kindly supplied by BASF.
4.3.2 Production of Meltspun PP Fibers with Nucleating Agent

Production of meltspun PP fibers with nucleating agent was accomplished through two steps. First, nucleating agent and polymer was melt pre-compounded to produce PP/nucleating agent master batch with 10 wt. % concentration of nucleating agent. In the next step, PP were mixed with different amount of the PP/nucleating agent masterbatch and melt extruded through the Hills Homofilament line to produce fibers with nucleating agent concentration of 0 (control), 0.001, 0.005, 0.01, 0.025, 0.05 and 0.1 wt. %. The produced meltspun fibers diameters were approximately 3 denier. The spinning speed, spin-head temperature and the melt throughput were 2000 m/min, 235 ºC and 0.6 g. hole.⁻¹ min⁻¹, respectively.

4.3.3 Differential Scanning Calorimetry Analysis

Crystallization and melting characteristics of meltspun fibers containing nucleating agent were studied using a TA Discovery differential scanning calorimeter under nitrogen atmosphere. Samples with average weight of 5-10 mg were heated from 25 ºC to 195 ºC and kept at 195 ºC for 5 min to remove their previous thermal history. Then they were cooled from 195 ºC to 25 ºC. For all these steps the heating and cooling rates were fixed on 10 ºC/min. The degree of crystallinity of fibers were determined with the following equation:

\[
\text{Crystallinity (\%) } = \frac{\Delta H}{\Delta H^0} \times 100
\]

(1)

where \(\Delta H\) stands for enthalpy of fusion of fibers (J/g) and \(\Delta H^0\) is defined as enthalpy of fusion of 100% crystalline PP polymer (207 J/g) ²⁶.
4.3.4 Isothermal Crystallization Analysis

The isothermal crystallization of meltspun fibers containing nucleating agent were also studied with TA Discovery differential scanning calorimeter. Samples were heated from 20 to 190 °C at the heating rate of 20 °C/min and they were maintained at 190 °C for 5 minutes. The next step was cooling down the samples at a rate of 50 °C/min to the temperature evaluated by adding of 5 °C to the observed onset crystallization temperature for each samples obtained from DSC analysis. Then samples maintained at that certain temperature for 10 minutes to be crystallized.

4.3.5 Wide-angle X-ray Diffraction Analysis (WAXD)

To evaluate the crystalline structure and crystal size of the samples, the WAXD tests were carried out with an Omni Instrumental Wide Angle X-Ray Diffractometer using the be-filtered Cu Kα radiation with a wavelength of 1.54 Å. The WAXD spectra were obtained at a voltage of 35 kV and 25 mA current. Samples were scanned in 2θ range of 5-40 (0.05 increments). The crystal size can be determined from scattering pattern according to Scherer’s equation \(^{22}\):

\[
t = \frac{0.9 \times \lambda}{B \times \cos \theta_B}
\]  

(2)

Where \(t\) represents the crystal size (Å), \(B\) is the full width at half- maximum (rad), \(\lambda\) is the wave length of X-ray (1.54 Å) and \(\theta_B\) is the Bragg angle.

4.3.6 Single-Fiber Tensile Testing

The tensile properties of meltspun fibers were measured with Favimat tensile testing machine according to ASTM D 1577 with the load cell of 210 cN and gauge length of 14 mm.
The rate of extension was maintained at 15 mm/min. The single fiber elongation, toughness and tenacity were evaluated from stress-strain curve and the average and standard error of 10 samples were reported.

4.4 Result and Discussion

4.4.1 Differential Scanning Calorimetry Analysis

*DSC Cooling Thermogram*

Thermal transition temperature for cooling thermogram of crystallization is highly influenced by presence of the nucleating agent in polymer (see figure 4.1).

![DSC Cooling Thermogram](image)

**Figure 4.1** : DSC cooling thermogram of PP meltspun fibers containing Iraeglear XT 386 (crystallization exotherm)
The crystallization graph indicates that as the Irgaclear XT 386 concentration increases to 0.005 wt. %, the onset crystallization temperature did not change and position of the peak remained the same as that of the PP fiber crystallization peak. But, as the Irgaclear XT 386 concentration increased to 0.01 wt. % the onset crystallization temperature increased to 126 °C. By further increasing the nucleating agent concentration, the onset crystallization temperature increased significantly from 126 °C for sample with 0.01 wt. % concentration of Irgaclear XT 386 to its maximum value 132 °C at 0.025 wt. % concentration of Irgaclear XT 386. The onset crystallization temperatures of all samples are given in table 4.1.

In fact, due to presence of nucleating agent there would be more nuclei in polymer melt and supersaturation happens from the very early stage of cooling process.

<table>
<thead>
<tr>
<th>Irgaclear XT 386 agent conc. (Wt. %)</th>
<th>Onset Crystallization Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP (0)</td>
<td>120</td>
</tr>
<tr>
<td>0.001</td>
<td>120</td>
</tr>
<tr>
<td>0.005</td>
<td>120</td>
</tr>
<tr>
<td>0.01</td>
<td>126</td>
</tr>
<tr>
<td>0.025</td>
<td>132</td>
</tr>
<tr>
<td>0.05</td>
<td>132</td>
</tr>
<tr>
<td>0.1</td>
<td>132</td>
</tr>
</tbody>
</table>

Therefore, for fibers containing Irgaclear XT 386 more crystals can be fashioned comparing to PP control fiber and the crystallization will start at higher temperature. The graph of
relative crystallinity versus temperature is created by converting the area under crystallization peak. As can be seen in figure 4.2, non-isothermal crystallization of PP fibers containing nucleating agent at a cooling rate of 10 °C/min shows the crystallization rate increased for fibers containing nucleating agent.

Therefore, the higher onset crystallization temperature can be attributed to higher rate of crystallization in presence of nucleating agent. So, to study the effect of nucleating agent on kinetic parameters the isothermal crystallization of samples were also studied and results are given in the next part.

![Graph showing relative crystallinity versus temperature](image)

**Figure 4.2**: Non-isothermal crystallization of PP meltspun fibers containing Iragclear XT

---

83
Isothermal Crystallization

The kinetic parameters for isothermal crystallization of samples were analyzed according to classical Avrami equation\(^\text{23}\):

\[
\ln \left[ -\ln \left( 1 - X_t \right) \right] = n \ln t + \ln k \quad (3)
\]

Where \(K\) is the Avrami crystallization rate constant, \(n\) is the Avrami exponent which indicates crystal growth mechanism and \(X_t\) stands for relative crystallinity at crystallization time \(t\). These parameters can be derived from the plot of \(\ln \left[ -\ln \left( 1 - X_t \right) \right]\) versus \(\ln t\). The Avrami plot of all samples is shown in figure 4.3. \(n\) and \(k\) values are obtained from the slope and intercept of the linear lines fitting of graphs in avrami plot, respectively and listed in table 4.2.

**Table 4.2**  
Isothermal crystallization kinetic parameters for PP meltspun fibers containing Irgaclear XT 386

<table>
<thead>
<tr>
<th>Irgaclear XT 386 agent conc. (Wt. %)</th>
<th>(n)</th>
<th>(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP (0)</td>
<td>2.5</td>
<td>0.09</td>
</tr>
<tr>
<td>0.001</td>
<td>2.7</td>
<td>0.07</td>
</tr>
<tr>
<td>0.005</td>
<td>2.5</td>
<td>0.07</td>
</tr>
<tr>
<td>0.01</td>
<td>3.0</td>
<td>0.03</td>
</tr>
<tr>
<td>0.025</td>
<td>2.3</td>
<td>0.11</td>
</tr>
<tr>
<td>0.05</td>
<td>2.7</td>
<td>0.12</td>
</tr>
<tr>
<td>0.1</td>
<td>2.6</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Results indicate as the Irgaclear XT 386 concentration increases from 0 to 0.01 wt. %, the \(k\) value decreases from 0.09 to 0.03.
Although for samples containing $\geq 0.025$ wt. % Irgaclear XT 386 the $k$ value as the overall rate of crystallization increased. The avarmi exponent $n$ value as the crystal growth mechanism for all samples are around 3.0, ranging between 2.3 and 3.0, which is attributed to three dimensional crystal growth.$^{28}$

![Avrami plot of ln (-ln (1-Xt)) versus ln t for PP meltspun fibers containing Irgaclear XT 386](image)

**Figure 4.3** : Avrami plot of $\ln (-\ln (1-Xt))$ versus $\ln t$ for PP meltspun fibers containing Irgaclear XT 386

**DSC Heating Thermogram**

According to DSC heating thermograms of fibers shown in figure 4.4, by application of nucleating agent the onset melting peak shape of samples slightly changed. Slight changes in
the shape of the melting peak can be due to change of fibers microstructure with addition of nucleating agent.

According to figure 4.4, for fiber samples containing 0, 0.001, 0.005 and 0.01 wt. % of nucleating agent, the melting peak is broad and consists of two distinct endotherm melting peaks. The first peaks at lower melting temperatures indicates creation of small imperfect crystals of fiber.

However, for samples containing 0.025, 0.05 and 0.1 wt. % of nucleating agent the melting peaks became narrower and less distinct. This can be attributed to narrower range of crystal sizes for samples with higher concentration of nucleating agent.\textsuperscript{23}

\textbf{Table 4.3} : DSC heating thermograms analysis of PP meltspun fibers containing Iragclear XT 386

<table>
<thead>
<tr>
<th>Nucleating agent conc. Wt. %</th>
<th>Onset Melting Temperature (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>154</td>
<td>46</td>
</tr>
<tr>
<td>0.001</td>
<td>154</td>
<td>48</td>
</tr>
<tr>
<td>0.005</td>
<td>154</td>
<td>48</td>
</tr>
<tr>
<td>0.01</td>
<td>154</td>
<td>46</td>
</tr>
<tr>
<td>0.025</td>
<td>155</td>
<td>46</td>
</tr>
<tr>
<td>0.05</td>
<td>158</td>
<td>44</td>
</tr>
<tr>
<td>0.1</td>
<td>158</td>
<td>44</td>
</tr>
</tbody>
</table>

Overall crystallinity is calculated from the total area of heating thermogram of the melting graph. As can be seen in figure 4.5, the crystallinity % did not change significantly with addition of nucleating agent.
This agrees other study about addition of nucleating agents in melt spinning of fibers.

**Figure 4.4:** DSC heating thermogram of PP meltspun fibers containing Iragclear XT 386 (melting endotherm)

**Figure 4.5:** The degree of crystallinity (%) for PP meltspun fibers containing Iragclear XT 386
Contrary to other polymeric materials, changes of crystallization kinetics via use of nucleating agents has not result in increasing crystallinity %. Application of nucleating agent for nylon 66 fibers did not show impact on crystallinity % of fibers.\textsuperscript{26}

According to another published study, addition of up to 3 wt. % concentration of nanoclay for developing melt spun PP fibers increase the rate of crystallization, but did not change crystallinity % of fibers.

### 4.4.2 Crystalline structure

During the melt spinning for fibers, a phase transition process where entangled polymer melt is transformed to the ordered complex microstructure semi-crystalline fibers occurs. So the developed fiber structure is highly influenced by crystallization process \textsuperscript{23}. Application of nucleating agent leads to alteration in crystallization kinetic and the fiber formation process. Consequently, fibers with different microstructure will be fashioned. Fibers crystalline morphology changes can be monitored via WAXD. WAXD patterns of neat PP fibers and PP fibers containing nucleating agent are shown in figure 4.6. According to the X-ray diffractogram of PP fiber, the crystalline peak is broad and occurs at a 2θ value of 16.3 which is corresponded to isotactic PP mesomorphic configuration \textsuperscript{23}. This broad peak suggests creation of not well-defined PP fiber crystalline structures.

Moreover, for samples containing 0.001, 0.005, 0.01 wt. % concentration of Irgaclear XT 386, the crystalline peaks are also broad at 2θ value of 16.4, 16.3 and 16 respectively. In fact, as the concentration of nucleating agent increases from 0 to 0.01 wt. % the diffraction peaks became sharper. Moreover, for fibers containing 0.025, 0.05 and 0.1 wt. % of Irgaclear XT 386, the X-ray diffractogram showed distinct crystalline peaks. For instance, with addition of
0.025 wt. % of nucleating agent the distinct crystalline peaks occurred at 2θ values of 15.0, 17.7, and 19.5 which is corresponded to the isotactic PP α-crystalline configuration. The more distinct peaks indicate formation of larger crystals. This can be attributed to creation of large amount of nuclei which impinges each other as they grow and/ or application of too much Irgaclear XT 386 additive. The crystal size, the interplanar d-spacing as well as the Bragg angle for each individual peak are listed in table 4.4.

<table>
<thead>
<tr>
<th>Nucleating agent conc. wt. %</th>
<th>2θ</th>
<th>d (Å)</th>
<th>Crystal size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>16.3</td>
<td>5.4</td>
<td>33</td>
</tr>
<tr>
<td>0.001</td>
<td>16.4</td>
<td>5.4</td>
<td>24</td>
</tr>
<tr>
<td>0.005</td>
<td>16.3</td>
<td>5.5</td>
<td>24</td>
</tr>
<tr>
<td>0.01</td>
<td>16.0</td>
<td>5.5</td>
<td>21</td>
</tr>
<tr>
<td>0.025</td>
<td>15.0</td>
<td>5.9</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>17.7</td>
<td>5.0</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>19.5</td>
<td>4.6</td>
<td>73</td>
</tr>
<tr>
<td>0.05</td>
<td>15</td>
<td>5.9</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>17.8</td>
<td>5.0</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>19.5</td>
<td>4.6</td>
<td>81</td>
</tr>
<tr>
<td>0.1</td>
<td>15</td>
<td>5.9</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>17.8</td>
<td>5.0</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>19.4</td>
<td>4.6</td>
<td>81</td>
</tr>
</tbody>
</table>

According to this table the crystals sizes decreased as the concentration of nucleating agent increased to 0.01 wt. %, while for fibers containing ≥ 0.025 wt. % of nucleating agent crystals sizes increased. These results are in good agreement with the ones obtained from DSC melting endotherm where onset melting temperature increased and melting peaks
became narrower that governs creation of larger crystallites and narrower range of crystal size for samples containing higher concentration of nucleating agent respectively.

![X-ray diffractogram of PP meltspun fibers containing Iragclear XT 386](image)

**Figure 4.6**: X-ray diffractogram of PP meltspun fibers containing Iragclear XT 386

### 4.4.3 Single Fiber Tensile Properties

Tensile behavior of fibers is governed by the polymeric chain properties such as chain rigidity, secondary bond strength between polymeric chain and molecular weight of the applied polymer. Moreover, microstructure of fibers fashioned through polymer chain alignment affects the tensile behavior of them. Since utilization of nucleating agent to make meltspun fibers results in significant changes in microstructure of fibers and polymer chain properties, so alteration of tensile behavior of fibers is expected. Application of nucleating
agent leads to significant changes in tensile properties. The single fiber elongation at break shown in figure 4.7, implicated that with addition of nucleating agent the single fiber elongation at break increased. In contrast, utilization of nucleating agent leads to lower tenacity of nucleating agent-PP fibers (figure 4.8). These phenomena might be due to change of polymer microstructure, formation of larger crystals and reduction of molecular orientation for samples containing nucleating agent. In fact, with addition of nucleating agent, crystallization tends to occur at a higher temperature closer to the spinneret, where the molecular orientation is lower in the melt so lower orientation for the product is expected. In this regard, decrease of modulus is quite possible due to reduction of molecular orientation, even though higher degree of crystallinity can be obtained in presence of nucleating agent.

Figure 4.7: Single fiber tensile property of PP meltspun fibers containing Iragclear XT 386 (elongation at break)
The effect of nucleating agent on fiber toughness was also studied. According to figure 4.9, addition of nucleating agent leads to increase in toughness. This may have been due to some fundamental microstructural changes and creation of larger crystals which can absorb and keep more energy before failure.
Effect of Irgaclear XT 386 nucleating agent on morphology and mechanical properties of meltspun PP fibers has been investigated. Results showed that, by application of Irgaclear XT 386 onset crystallization temperature of polymers increased. However, according to DSC heating thermogram of fibers, crystallinity % of samples did not change significantly with addition of nucleating agent.

WAXD study indicated that, for samples containing lower concentration of nucleating agent (0.001-0.01 wt. %) crystals sizes decreased compared to crystals sizes of PP control sample. This is similar to what normally happens in case of application of nucleating agent for making polymeric films. However, for samples with higher concentration of nucleating agent (0.025-0.1 wt. %) crystal size increased. According to DSC isothermal analysis, rate of
crystallization increased for fibers with $\geq 0.025$ wt. % nucleating agent. Also, fibers containing nucleating agent exhibited higher elongation at break and toughness and lower tenacity compared to PP control fibers. Although these tensile properties followed contrary trend as the nucleating agent concentration increased to 0.1 wt. %.
4.6 References


5. The effect of 1,3,5-tris(2,2-dimethylpropionylamino)benzene on morphology and filtration performance of polypropylene meltblown nonwovens

5.1 Abstract

Meltblown polypropylene nonwovens with different concentration of 1,3,5-tris(2,2-dimethylpropionylamino)benzene (commercially known as Irgaclear XT 386) nucleating agent were produced by meltbowing process. The effect of this nucleating agent on crystallization behavior, crystalline and web structure and filtration properties of the produced meltblown nonwovens was investigated. Results indicate application of Irgaclear XT 386 in meltblowing process, leads to higher onset crystallization temperature of polymer, increase of crystallinity (%), change of crystalline structure, lower solidity, higher air permeability and improved filtration performance of developed meltblown nonwovens. 

Key words: Meltblown, nonwoven, polypropylene, nucleating agent, morphology, filtration performance

5.2 Introduction

Polymers electret properties privileged several high-tech inventions including aerosol filters, electret ion chambers, microphones and radiation sensors. Most studies were focused on improving electret properties of films, but recently, research has been conducted to study the effect of electret additives on polarization properties of polymers and electret properties of fiber-based devices \(^{1,2}\).
Electret filter is an example of fiber-based devices which found technical and commercial interests lately. Electret filters filtration efficiency is highly dominated by the electret field strength of the fibrous media. In this regard, charge stability is very important since high initial charge density does not guarantee high charge stability. In fact, loss of charge can lead to significant decrease of filter media total filtration performance \(^3\)–\(^6\). Additives can be used to improve both charge density and stability, however, there is no specific additive designed specifically for this purpose. In this regard, nucleating agents, light stabilizers, fluorochemicals, inorganic additives, and antioxidants can be used to improve charge retention and stability \(^7\). In the case of filters, loss of charge can be attributed to creation of conductive film upon filtration \(^8\)–\(^10\). Fluorochemicals have been used to prevent conductive film formation and charge decay \(^3\). According to recent investigations, application of BaTiO\(_3\) as an additive with high dielectric constant in PP meltblown nonwovens led to improved charging and filtration properties of the developed PP electret nonwoven filters \(^7\). Moreover, charge retention and stability of the studied electret filters was promising. Also, morphology of the fibers did not change significantly with addition of BaTiO\(_3\) \(^7\). Uniformly and thermally charged samples showed superior and stable electret filtration properties. Accelerated decay test was applied for PP nonwoven filters containing over 1% BaTiO\(_3\) \(^7\). Results showed both filtration efficiency and charge stability of filters increased significantly. Moreover, filtration performance of nonwoven filters containing over 1% BaTiO\(_3\) did not alter significantly after isothermal decay test \(^7\).

Beside dielectric additives, nucleating agents can be applied to improve electret properties of polymeric films \(^1\),\(^11\)–\(^17\).
According to previous studies, nucleating agents showed potential to enhance electret properties of polymeric products. Application of nucleating agent leads to formation of small spherulites whose boundaries act as traps for space charges. Moreover, microvoids can be generated upon addition of nucleating agents which prohibits charge migration. Unlike some other additives, nucleating agents can be buried into crystallites where charge stability is better than the amorphous regions. Different types of nucleating agents such as trisamide and its derivatives, sodium 2,2'-methylene bis (4,6-di-terbutylphenyl)-phosphate (NA11), bisamide, N,N'-dicyclo-haxyl-2,6-naphthalene-dicarbox-amide (NU100) and etc. have been examined as electret additives. Effect of 1,4-phenylene bisamides as crystal nucleators on chargeability of PP film was investigated. Nucleation ability as well as PP film charge stability was disturbed in presence of bisamides containing long aliphatic side chains. Symmetry and concentration of additives play important roles on electret properties of the final products. However, concentration showed more impact on charge stability. It is suggested that, application of below 0.05 Wt. % concentration of bisamide additives for PP films resulted in 20% increase of charge stability compared to the remained potential after annealing (at 90 ºC for 24 hrs.). At higher concentrations of nucleating agent, not only the network will be formed but also aggregation of insoluble additive happens because of the percolation.

Similarly, application of 0.04 wt. % (high concentration) triphenylamine based trisamides provides sufficient quantities of charge carriers to provide high conductivity. Presence of –NH groups in amide containing trisamides leads to formation of macrodipoles and consequently enhanced charge retention of the host polymer. Trisamides without amide
groups showed worst stability than the pure films. In fact, percolation can happen at higher concentrations where larger 3D network structure is fashioned \(^\text{17}\).

On the other hand, application of nucleating agents like NA11 that does not dissolve in PP may lead to the formation of micro-voids during the film manufacturing process \(^\text{1,12}\). In this case, electret properties depend on the fashioned elongated voids which are considered as potential charge barriers against decay. Charge stability of polymeric films containing NA11 can be improved upon stretching due to formation of more cavities in presence of nucleating agent \(^\text{1,12}\).

It was observed that, in the case of application of below 0.5 wt. % concentration of NU100, charge decay was faster compared to the pure iPP \(^\text{2}\). This happens due to formation of the 3D network structure pathways for charge carriers provided by hydrogen bonds \(^\text{17}\). Antioxidants can be applied as nucleating agents and render deep charge traps \(^\text{17}\).

Effect of commercially available nucleating agents including NA11 and DMDBS was studied on PP fibers and nonwovens filtration and charging properties \(^\text{2,3}\). For nonwovens containing these nucleating agents, samples were charged at both room and elevated temperatures to investigate the effect of nucleating agents on charging properties of PP nonwovens \(^\text{2}\). Thermally charged webs containing nucleating agents provided not only enhanced electrostatic potential but also improved filtration properties. These improvements are attributed to higher potential values originated from dielectric properties of the mentioned nucleating agents. This is the reason that additives with high polarizability are suitable candidates for improving both charge density and stability of materials \(^\text{2}\). In the case of addition of those mentioned nucleating agents for fibers, NA11 showed more impact on
charge stability while samples containing DMDBS showed more decay\(^2\). However, upon charging at elevated temperature of samples containing NA11 and DMDBS, charge density and stability improved. Cold charging was not an effective method to improve electret properties. Polarization of these additives molecules is the main reason behind enhanced charge density and stability of the developed materials\(^2\). The trisamide derivative Irgaclear XT 386 used in this study contains amide linkages which are able to build strong hydrogen bonds. Therefore, it is claimed that, they are thermally and chemically stable in different environments unlike sorbitol derivatives\(^{20}\). By application of small amount (\(~100\text{-}200\text{ ppm}\)) of the noticed melt sensitive trisamide derivative, a finely distributed crystalline domain will be formed upon cooling which provides a huge nucleation surface for the crystallization process\(^{21,22}\). In this regard, utilization of very low concentration of Irgaclear XT 386 can lead to decreased spherulite size, higher rate of crystallization and degree of crystallinity, improved electret, optical and physical properties of the developed polymeric materials like films\(^{23\text{-}26}\). In this study, to investigate the effect of nucleating agent on morphology and filtration properties of meltblown nonwoven, 1,3,5-tris(2,2-dimethylpropionylamino) nucleating agent (commercially known as Irgaclear XT386) is used to develop PP meltblown webs.

5.3 Materials and Methods

5.3.1 Materials

A commercially available PP (Metosene MF650W) with melting index of 500g/10 min used for this study was provided by LyondellBasell. The 1,3,5-tris(2,2-
dimethylpropionylamino)benzene nucleating agent commercially known as Irgaclear XT386 in powder form was purchased from BASF.

**5.3.2 Production of Meltblown PP-Nucleating Agent Nonwovens Web**

PP- nucleating agent meltblown webs were produced with Reicofil meltblown machine at the nonwovens institute/ North Carolina state university.

Preparation of meltblown PP webs containing nucleating agent was accomplished through two steps. First, nucleating agent and polymer was melt pre-compounded to produce PP/nucleating agent master batch with 10 wt. % concentration of nucleating agent. In the second step, PP were mixed with different amount of the PP/nucleating agent masterbatch and melt extruded through the Reicofil meltblown machine to produce meltblown webs with nucleating agent concentration of 0 (control), 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4 and 0.5 wt. %. The meltblown die used for this study was an Exxon die with 35 holes per inch. During meltblowing process the die to collector distance (DCD), air flow and polymer throughput were fixed at 0.25 m, 1100 m$^3$/hr and 0.5 g hole$^{-1}$ min$^{-1}$, respectively to produce nonwoven webs with 40 gm$^{-2}$ basis weight. During the meltblowing process, polymer/die temperature and die air temperature were 250 ºC and 260 ºC, respectively. In figure 5.1 schematic of Reicofil meltblown machine is shown.
5.3.3 Differential Scanning Calorimetry Analysis

Crystallization and melting characteristics of meltblown webs containing nucleating agent were studied using a TA Discovery differential scanning calorimeter under nitrogen atmosphere. Samples with average weight of 5-10 mg were heated from 25 °C to 195°C and kept at 195 °C for 5 min to remove their pervious thermal history. Then they were cooled from 195 °C to 25 °C. In all mentioned steps, the heating and cooling rates were maintained at 10 °C/min.
Melting characteristics of meltblown webs containing nucleating agent were studied using a TA Discovery Modulated Differential Scanning Calorimeter (MDSC) under nitrogen atmosphere. Samples with average weight of 10-15 mg were heated from 25 °C to 200°C with heating rate of 2 °C/min, modulation amplitude of 0.318 °C and modulation period of 60 seconds. 

Crystallinity % of the meltblown webs were evaluated as follows:

\[
\text{Crystallinity (\%) = } \frac{\Delta H}{\Delta H^0} \times 100 \quad (1)
\]

Where \( \Delta H \) stands for enthalpy of fusion for fibers (J/ g) and \( \Delta H^0 \) is defined as enthalpy of fusion for 100% crystalline PP polymer (207 J/g)\(^{22}\).

### 5.3.4 Wide-angle X-ray Diffraction Analysis (WAXD)

To evaluate the crystalline structure and crystal size of the samples, WAXD tests were carried out with an Omni Instrumental Wide Angle X-Ray Diffractometer using the be-filtered Cu Kα radiation with a wavelength of 1.54 A°. The WAXD spectra were obtained at a voltage of 35 kV and 25 mA current. Samples were scanned in the 2θ range of 5-40 (0.05 increments). The crystal size can be determined from scattering pattern according to Scherer’s equation\(^{27}\):

\[
t = \frac{0.9 \times \lambda}{B \cos \theta_B} \quad (2)
\]

Where \( t \) represents the crystal size (A°), \( B \) is the full width at half- maximum (rad), \( \lambda \) is the wave length of X-ray (1.54 A°) and \( \theta_B \) is the Bragg angle.
5.3.5 Web properties

Meltblown web properties including web basis weight, thickness, solidity and fiber diameter play important roles on the performance of nonwovens. Webs basis weights were measured according to ASTM D3776 and average basis weight measured for 5 samples were reported in g/m$^2$. Nonwovens thickness was evaluated according to ASTM D1777 by using Precision Thickness Gauge-FT3 (Hanatek Instruments). The average thickness measured for 10 samples were reported in µm. Solid volume fraction of samples are evaluated by using the obtained basis weight and thickness for each sample according to following equation $^2$:

$$\text{Solidity} = \frac{\text{basis weight}}{\text{thickness} \times \text{density}}$$

To evaluate fiber diameter for each sample, first it was coated with a thin layer of gold and then SEM images were taken with JEOL 7600F scanning electron microscope at AIF, NCSU $^{28}$. The average fiber diameter measured for 100 fibers were reported in µm.

5.3.6 Filtration Properties

Filtration properties of meltblown webs were measured by using TSI (3160) filtration testing machine where nonwoven webs were exposed to dioctylphthalate (DOP) aerosols with particle size of 0.3 µm at a face velocity of 5.3 cm/s. The TSI 3160 atomizer bank generates the aerosol which will be evaporated through a membrane dryer. The upstream and downstream particles are concurrently counted with Two Condensation Particle Counters (CPCs) and the penetration value is measured by the computer software and summary of test results such as penetration vs. particle size is generated.
Quality factor as the filtration index of nonwovens relates aerosol capture efficiency to the pressure drop and is calculated according to the following equation \(^2\):

\[
\text{Quality factor (QF)} = \frac{-\ln(P)}{\Delta P}
\]

where \(P\) is the penetration (1-efficiency) and \(\Delta P\) stands for pressure drop.

As it is known chargeability of samples is important but stability of those charges is very critical as well. Therefore the decay test was performed through which all samples were charged with corona discharger and then they were placed in the environmental chamber at 70\(^\circ\)C temperature and 50\% humidity for 1 and 2 hours decay time. After annealing, samples were cooled for 10 minutes and then filtration efficiencies were measured.

### 5.3.7 Charging

Nonwoven samples were charged with a corona discharger (Mystic Marvels, Model NIP-7E) at room temperature where the applied voltage was 22 kV for 60 seconds on the back and front sides of samples. The distance between the sample and discharger was fixed at 3 cm.

### 5.4 Result and Discussion

#### 5.4.1 Differential Scanning Calorimetry (DSC) Analysis

**DSC Cooling Thermogram**

Thermal transition temperature for cooling thermogram of crystallization is affected by presence of nucleating agent in polymer. The cooling graph indicates that as the Irgaclear XT 386 concentration increases to 0.01 wt. \%, onset crystallization temperature of polymer increased by 10 \(^\circ\)C to its maximum value 130 \(^\circ\)C and the peak of crystallization exotherm shifted to right (see figure 5.2).
By further increasing the nucleating agent concentration, onset crystallization temperature did not change. Onset crystallization temperatures of all samples are given in Table 5.1. In fact, by application of nucleating agent and presence of more nuclei in polymer melt, supersaturation occurs from the very early stage of cooling process and crystallization will start at higher temperature.

**Figure 5.2**: DSC cooling thermogram of PP nonwovens containing Irgaclear XT 386 (crystallization exotherm)
Table 5.1: Isothermal crystallization kinetic parameters of nonwovens containing Irgaclear XT 386

<table>
<thead>
<tr>
<th>Nucleating agent conc. wt. %</th>
<th>Onset crystallization temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP (0)</td>
<td>120</td>
</tr>
<tr>
<td>0.01</td>
<td>130</td>
</tr>
<tr>
<td>0.02</td>
<td>130</td>
</tr>
<tr>
<td>0.03</td>
<td>130</td>
</tr>
<tr>
<td>0.04</td>
<td>130</td>
</tr>
<tr>
<td>0.05</td>
<td>130</td>
</tr>
<tr>
<td>0.06</td>
<td>130</td>
</tr>
<tr>
<td>0.07</td>
<td>130</td>
</tr>
<tr>
<td>0.08</td>
<td>130</td>
</tr>
<tr>
<td>0.09</td>
<td>130</td>
</tr>
<tr>
<td>0.1</td>
<td>130</td>
</tr>
<tr>
<td>0.2</td>
<td>130</td>
</tr>
<tr>
<td>0.3</td>
<td>130</td>
</tr>
<tr>
<td>0.4</td>
<td>130</td>
</tr>
<tr>
<td>0.5</td>
<td>130</td>
</tr>
</tbody>
</table>

Crystallinity % from Modulated DSC Heating Thermogram

Crystallinity (%) of meltblown nonwovens were evaluated from modulated DSC heating thermogram. As can be seen in figure 5.3, crystallinity % increased as the nucleating agent concentration increased to 0.3 wt. %. At higher concentrations of nucleating agent such as 0.4 and 0.5 wt. %, crystallinity % started to decrease, although it remained higher compared to PP meltblown nonwoven crystallinity %.
5.4.2 Crystalline structure

Application of nucleating agent can lead to alteration in crystallization kinetic, fiber and nonwoven formation during the meltblowing process. Consequently, nonwovens with different microstructure will be fashioned. Nonwovens crystalline morphology changes can be monitored via WAXD. WAXD patterns of PP meltblown nonwoven containing 0, 0.01 wt. % (lowest concentration of nucleating agent) and 0.5 wt. % (highest concentration of nucleating agent) are shown in figure 5.4. According to the X-ray diffractogram, for PP meltblown control nonwoven the crystalline peaks are broad and occur at a 2θ value of 14.5255, 17.8676, 19.7144 and 22.6505 which are correspondent to α crystalline form of isotactic PP. However, for nonwovens containing nucleating agent, crystalline peaks are sharper and more distinct which suggest formation of well-shaped crystals in presence of nucleating agent.
The crystal size, the Bragg angle as well as Full Width at Half Maximum (FWHM) for each individual peak are listed in table 5.2. According to this table, for nonwovens containing 0.01 wt. % concentration of nucleating agent, crystals sizes decreased compared to the PP control nonwoven. However, as the concentration of nucleating agent increased to 0.5 wt. %, crystals sizes increased compared to nonwovens containing 0.01 wt. % concentration of nucleating agent, although they remained smaller than the PP control nonwoven crystals sizes.

Figure 5.4: X-ray diffractogram of PP meltblown nonwoven containing Iragclear XT 386
The reason behind this phenomenon could be utilization of too much additive that can lead to agglomeration and formation of larger crystals sizes.

**Table 5.2**: Crystallite size of PP meltblown nonwoven containing Iragclear XT 386

<table>
<thead>
<tr>
<th>Nucleating agent conc. wt. %</th>
<th>2θ</th>
<th>FWHM (radian)</th>
<th>Crystal size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15.2</td>
<td>1.02</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>17.9</td>
<td>0.271</td>
<td>296</td>
</tr>
<tr>
<td></td>
<td>19.7</td>
<td>0.145</td>
<td>552</td>
</tr>
<tr>
<td></td>
<td>22.7</td>
<td>0.689</td>
<td>118</td>
</tr>
<tr>
<td>0.01</td>
<td>15.1</td>
<td>1.112</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>17.7</td>
<td>0.820</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>19.5</td>
<td>0.383</td>
<td>210</td>
</tr>
<tr>
<td>0.5</td>
<td>15.6</td>
<td>0.771</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>18.4</td>
<td>0.245</td>
<td>281</td>
</tr>
<tr>
<td></td>
<td>19.9</td>
<td>0.805</td>
<td>100</td>
</tr>
</tbody>
</table>

**5.4.3 Web Properties**

As it was discussed, according to DSC analysis, with addition of nucleating agent onset crystallization temperature of polymer increased. It is expected that, increase of onset crystallization temperature of polymer in presence of nucleating agent may lead to faster solidification of polymer melt closer to the meltblowing die face and formation of bulkier structure nonwovens with higher air permeability and lower solidity. In this regard both solidity and air permeability of all webs were evaluated. As can be seen in figure 5.5, with
Figure 5.5: Effect of Irgaclear XT 386 on solidity of meltblown nonwovens

Figure 5.6: Effect of Irgaclear XT 386 on air permeability of meltblown nonwovens
addition of nucleating agent solidity of nonwovens increased while according to figure 5.6 air permeability of them increased.

Results showed by application of Irgaclear XT 386 in melt blowing process, solidification of polymer melt can happen faster and lead to formation of bulkier structure nonwovens with lower solidity and higher air permeability which privilege low pressure drop in case of air filtration applications of nonwovens.

According to SEM images shown in figure 5.7 (a, b) and figure 5.8, with addition of nucleating agent mean fiber diameter slightly increased. The slight increase of mean fiber diameter can be attributed to faster solidification of polymer melt closer to the meltblowing die face in presence of nucleating agent.

![SEM images of fibers](image)

**Figure 5.7**: a) Fibers in PP meltblown nonwoven, b) Fibers in PP meltblown nonwoven containing 0.02 wt. % conc. of Irgaclear XT 386
5.4.4 Filtration Properties

Filtration test was performed for as received nonwovens including PP control nonwoven and all the nonwovens containing nucleating agent. Then all of them were charged positively with the corona discharger and again filtration efficiencies were measured using TSI testing machine. In this regard, filtration performance of PP control nonwoven and samples containing nucleating agent can be compared before and after charging. According to figure 5.9, for as received nonwovens, for samples with lower concentration of nucleating agent, filtration efficiency increases from ~ 23 % for PP control nonwoven to ~ 28% for nonwoven containing 0.1 wt. % of nucleating agent while pressure drop decreased.
Moreover, for nonwovens with higher concentration of nucleating agent like 0.5 wt. %, filtration efficiency did not change significantly compared to the PP control nonwoven but pressure drop decreased a lot. The decrease of pressure drop can be attributed to lower solidity of nonwovens with higher concentration of nucleating agent. In other words, as it is shown in figure 5.10, quality factor as the filtration index of nonwovens increased for samples containing Irgaclear XT 386.
Upon charging, filtration efficiency of all nonwovens increased by ~ 60% (see figure 5.11).

As it is known chargeability of samples is important but stability of those charges is very critical as well. Therefore, decay test was performed at elevated temperature (70 °C) and 50 % humidity.
The normalized charge retention efficiency was measured as follows:

Normalized charge retention efficiency = \( \frac{\text{Efficiency of charged web after certain time decay}}{\text{Efficiency of charged filter before decay}} \times 100 \)

According to figure 5.12, for PP control nonwoven most of the decay happened at the first 1 hour decay time. But for samples containing Irgaclear XT 386, specially the one with 0.1 wt. % concentration of nucleating agent charge retention remained very high, almost close to 100.
These different behaviors can be related to different crystalline structure of samples. According to WAXD analysis shown in figure 5.4, for nonwoven containing 0.1 wt. % concentration of Irgaclear XT 386 crystalline peak are sharper and more distinct which suggests formation of well-shaped crystals in presence of nucleating agent. Also, crystals sizes of nonwoven containing 0.1 wt. % concentration of nucleating agent is smaller compared to crystals sizes of PP control nonwoven. In this regard, the increased charge retention of nonwoven containing 0.1 wt. % concentration of nucleating agent can be attributed to smaller well-shaped crystals sizes which result in larger crystal amorphous boundaries where space charges are located.

**Figure 5.12**: Normalized charge retention efficiency for pp control nonwoven and nonwovens containing Irgaclear XT 386 after 0, 0.5, 1 and 2 hrs. decay times
5.5 Conclusion

Effect of Irgaclear XT 386 nucleating agent on morphology and filtration properties of PP meltblown nonwovens has been investigated. Results showed that, by application of Irgaclear XT 386 onset crystallization temperature of polymers increased by 10 °C. Moreover, crystallinity % of samples increased as the Irgaclear XT 386 concentration increased from 0 to 0.3 wt.%, while for higher concentration of nucleating agent, crystallinity % decreased. Although, at very high concentrations (0.4 and 0.5 wt. %) crystallinity % were still higher compared to PP control nonwoven crystallinity %. WAXD analysis indicated that, for samples containing very low concentration of nucleating agent (0.01 wt. %) crystals sizes are smaller compared to crystals sizes of PP control nonwoven. This is similar to what normally happens in case of application of nucleating agent for polymeric films. However, for samples very high concentration of nucleating agent (0.5 wt. %) crystals sizes increased compared to nonwoven containing 0.01 wt. % concentration of nucleating agent, although they remained smaller than the PP control nonwoven crystals sizes. Moreover, increase of onset crystallization temperature of polymer in presence of nucleating agent led to faster solidification of polymer melt and formation of bulkier structure nonwovens with lower solidity, higher air permeability and improved filtration properties.
5.6 References


6. The Structure-Property-Process Relationship in Nonwovens Containing 1,3,5-tris(2,2 dimethylpropionylamino)benzene

6.1 Abstract

To understand the structure-property-processing relationships of polypropylene (PP) meltblown nonwovens containing 1,3,5-tris(2,2-dimethylpropionylamino)benzene (commercially known as Irgaclear XT 386) nucleating agent, meltblown nonwovens were produced with Recofil meltblown machine. In this study, the meltblown process parameters including Die to Collector Distance (DCD) and die air temperature were considered as process variables while other processing parameters were kept constant. So, meltblown webs with 0 and 0.02 wt. % concentration of Irgaclear XT 386 were produced through meltblowing process and then analysed with different techniques such as Differential Scanning Calorimeter (DSC), Modulated Differential Scanning Calorimeter (MDSC), Wide Angle X-ray Diffraction (WAXD), Scanning Electron Microscopy (SEM) and etc.

Results indicate increase of DCD in meltblowing of polymer containing Irgaclear XT 386 resulted in decrease of crystal size, increase of crystallinity % and higher air permeability of webs; whereas increase of die air temperature led to change of crystalline structure, decrease of crystallinity % and lower air permeability of meltblown nonwovens.

**Key words:** Meltblown, nonwoven, polypropylene, nucleating agent, Die to Collector Distance (DCD), die air temperature
6.2 Introduction

Application of nucleating agents for crystallization from quiescent polymer melt results in higher degree of crystallinity and onset crystallization temperature of polymers, higher thermal stability, improved electret, optical and physical properties of the developed materials like polymeric films. Also, in melt spinning process, application of nucleating agent can affect onset crystallization temperature of polymers and crystallinity % of fibers. In melt spinning process, crystallization is governed not only by super cooling but also by stress. At higher spinline stress, rate of crystallization is very high and effect of nucleating agent would not be very impressive, although it is not completely eliminated. In this regard, nucleating agent influence might be more pronounced at low spinning speeds. At low spinning speeds, since the driving force for crystallization is not large enough, the developed fiber has intermediate orientation with no or very low degree of crystallinity. In this case, crystallization probably can be influenced by nucleating agents. With addition of nucleating agent, crystallization tends to occur at a higher temperature closer to the spinneret, where the molecular orientation is lower in the polymer melt. Therefore, lower molecular orientation of the product is expected. In this regard, due to reduction of molecular orientation, decrease of modulus is quite possible. Reduction of molecular orientation in presence of nucleating agent may lead to higher elongation at break of the developed fibers. Nucleating agent is reported to be effective in increasing the porosity as well as water flux of PP fiber membrane made through melt spinning process. Also according to another study, with addition of up to 3 wt. % concentration of nanoclay for developing melt spun PP fibers, onset crystallization temperature of polymer increased
while crystallinity % of the fibers did not changed significantly. Application of nucleating agent for nylon 66 fibers led to decrease of induction time and higher rate of crystallization while it did not show impact on crystallinity % of fibers.

For meltblowing process, application of nucleating agent may lead to faster solidification of polymer melt and higher air permeability of webs. Moreover, nucleating agent can impact electret properties of the nonwovens. Effect of commercially available nucleating agents including NA11 and DMDBS was studied on PP fibers and nonwovens properties. In the case of nonwovens containing the noticed nucleating agents, solidity of webs decreased while air permeability of them increased. Moreover, samples were charged at both room and elevated temperatures to investigate the effect of nucleating agents on charging properties of PP nonwovens. Thermally charged webs containing nucleating agents, provided not only enhanced electrostatic potential but also improved filtration properties. These improvements are attributed to higher potential values originated from dielectric properties of NA11 and DMDBS nucleating agents. This is the reason that additives with high polarizability are suitable candidates for improving both charge density and stability of materials.

According to another study, application of 0.04 wt. % (high concentration) triphenylamine based trisamides provides sufficient quantities of charge carriers to provide high conductivity. Presence of –NH groups in amide containing trisamides leads to self-assembly, formation of macrodipoles and consequently enhanced charge retention of the host polymer. Trisamides without amide groups showed worst stability than the pure films. In fact, percolation can happen at higher concentrations where larger 3D network structure is fashioned.
According to previous chapter, by application of 1,3,5-tris(2,2-dimethylpropionylamino) (Irgaclear XT 386) as the meltblowing material variable in polymer, crystallization starts at higher temperature which affects structure and properties of the developed nonwovens. Beside material variable, change in the melblowing process variable might lead to alteration in structure and properties of the developed webs containing nucleating agent. In this regard, the meltblown machine Die to Collector Distance (DCD) and die air temperature were considered as the meltblowing process variables. In fact, change of each of these variables along with the presence of nucleating agent can affect crystallization and therefore properties of the developed webs.

Therefore, to explore the structure-property-processing relationship in meltblown nonwovens containing nucleating agent, Irgaclear XT386 and PP were used as materials. In this study, Die to Collector Distance (DCD) and die air temperature were considered as meltblowing process variables while other processing parameters were kept constant. So, meltblown nonwovens with 0 and 0.02 wt. % concentration of Irgaclear XT 386 were produced with Reicofil meltblown machine and then analyzed with different techniques such as Differential Scanning Calorimeter (DSC), Modulated Differential Scanning Calorimeter (MDSC), Wide Angle X-ray Diffraction (WAXD), Scanning Electron Microscopy (SEM) and etc.
6.3 Materials and Methods

6.3.1 Materials

PP (Metocene MF605W) with Melting index of 500g/10 min used for this study was provided by LyondellBasell. The 1,3,5-tris(2,2-dimethylpropionylamino)benzene nucleating agent commercially known as Irgaclear XT386 was kindly supplied by BASF.

6.3.2 Production of PP-Nucleating agent Meltblown Nonwovens Web

PP- nucleating agent meltblown nonwoven webs were produced with Reicofil meltblown machine at the nonwovens institute/ North Carolina state university. Preparation of meltblown PP nonowvens containing nucleating agent was accomplished through two steps. First, nucleating agent and polymer was melt pre-compounded to produce PP/nucleating agent master batch with 10 wt. % concentration of nucleating agent. In the second step, PP were mixed with different amount of the PP/nucleating agent masterbatch and melt extruded through the Reicofil meltblown machine to produce meltblown webs with 0 and 0.02 wt. % concentration of nucleating agent. In this regard, to investigate the effect of die air temperature during meltblowing process, DCD, air flow, polymer throughput and polymer/die temperature were set at 15 cm, 1100 m$^3$/hr., 0.5 g hole$^{-1}$ min$^{-1}$ and 250 °C, respectively to produce nonwoven webs with 40 gm$^{-2}$ basis weight. In this experiment, effect of different die air temperatures including 255, 265 and 275 °C was studied in meltblowing of polymer containing Irgaclear XT 386 (see table 6.1).
Table 6.1: The sample specification in investigating the effect of die air temperature in meltblowing of polymer containing Irgaclear XT 386

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Web basis weight (g m(^{-2}))</td>
<td>40</td>
</tr>
<tr>
<td>DCD (cm)</td>
<td>15</td>
</tr>
<tr>
<td>Throughput (g hole(^{-1}) min(^{-1}))</td>
<td>0.5</td>
</tr>
<tr>
<td>Air flow (m(^3)/hr)</td>
<td>1100</td>
</tr>
<tr>
<td>Die/polymer temperature (°C)</td>
<td>250</td>
</tr>
<tr>
<td>Die air temperature (°C)</td>
<td>255, 265, 275</td>
</tr>
<tr>
<td>Nucleating agent conc. (wt. %)</td>
<td>0, 0.02</td>
</tr>
</tbody>
</table>
Table 6.2: The sample specification in investigating the effect of DCD in meltblowing of polymer containing Irgaclear XT 386

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Web basis weight (g m⁻²)</td>
<td>40</td>
</tr>
<tr>
<td>Die air temperature (°C)</td>
<td>255</td>
</tr>
<tr>
<td>Throughput (g hole⁻¹ min⁻¹)</td>
<td>0.5</td>
</tr>
<tr>
<td>Air flow (m³/hr)</td>
<td>1100</td>
</tr>
<tr>
<td>Die/polymer temperature (°C)</td>
<td>250</td>
</tr>
<tr>
<td>DCD (cm)</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>35</td>
</tr>
<tr>
<td>Nucleating agent conc. (wt. %)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
</tr>
</tbody>
</table>

6.3.3 Differential Scanning Calorimeter Analysis

Crystallization and melting characteristics of meltblown webs containing nucleating agent were studied using a TA Discovery differential scanning calorimeter under nitrogen atmosphere. Samples with average weight of 5-10 mg were heated from 25 °C to 195°C and kept at 195 °C for 5 min to remove their previous thermal history. Then they were cooled
from 195˚C to 25 °C. In all mentioned steps, the heating and cooling rates were maintained at 10 °C/min.

Melting characteristics of meltblown webs containing nucleating agent were studied using a TA Discovery modulated differential scanning calorimeter under nitrogen atmosphere. Samples with average weight of 10-15 mg were heated from 25 °C to 200˚C with heating rate of 2 °C/min, modulation amplitude of 0.318 °C and modulation period of 60 seconds.

Crystallinity % of the meltblown webs were evaluated as follows:

$$\text{Crystallinity (\%) = } \frac{\Delta H}{\Delta H^0} \times 100 \quad (1)$$

Where $$\Delta H$$ stands for enthalpy of fusion for fibers (J/ g) and $$\Delta H^0$$ is defined as enthalpy of fusion for 100% crystalline PP polymer (207 J/g) 6.

### 6.3.4 Wide-angle X-ray Diffraction Analysis (WAXD)

To evaluate the crystalline structure and crystal size of the samples, the WAXD tests were carried out with an Omni Instrumental Wide Angle X-Ray Diffractometer using the be-filtered Cu Kα radiation with a wavelength of 1.54 Å. The WAXD spectra were obtained at a voltage of 35 kV and 25 mA current. Samples were scanned in the 2θ range of 5-40 (0.05 increments). The crystal size can be determined from scattering pattern according to Scherer’s equation 5:

$$t = \frac{0.9 \times \lambda}{B \times \cos \theta_B} \quad (2)$$

Where t represents the crystal size (Å), B is the full width at half- maximum (rad), λ is the wave length of X-ray (1.54 Å) and $$\theta_B$$ is the Bragg angle.
6.3.5 Web Properties

Meltblown nonwovens properties including basis weight, thickness, solidity and fiber diameter play important roles on the performance of webs. Nonwovens basis weights are measured according to ASTM D3776 and average basis weight measured for 5 samples are reported in g/m². Webs thicknesses are evaluated according to ASTM D1777 by using Precision Thickness Gauge-FT3 (Hanatek Instruments). The average thickness measured for 10 samples are reported in µm. Solid volume fractions are evaluated by using the obtained basis weight and thickness of each sample according to following equation 7:

\[
\text{Solidity} = \frac{\text{basis weight}}{\text{thickness} \times \text{density}}
\]

To evaluate fiber diameter of nonwovens, first it is coated with thin layer of gold and then SEM images are taken with JEOL 7600F scanning electron microscope at AIF, NCSU. The average fiber diameter measured for 100 fibers are reported in µm.

6.4 Result and Discussion

6.4.1 Effect of Die Air Temperature on PP Meltblown Webs Containing Irgaclea XT 386

6.4.1.1 Differential Scanning Calorimetry (DSC) Analysis

DSC Cooling Thermogram

Thermal transition temperature for cooling thermogram of crystallization is affected by presence of nucleating agent in polymer.
The cooling graph indicates that as the Irgaclear XT 386 concentration increases to 0.02 wt. %, onset crystallization temperature increased by 10 ºC to its maximum value 131 ºC (see figure 6.1).

![Figure 6.1](image)

**Figure 6.1**: DSC cooling thermogram of PP meltblown nonowvens and PP meltblown nonowvens containing Irgaclear XT 386 at different die air temperatures (crystallization exotherm)

In fact, by application of nucleating agent and presence of more nuclei in polymer melt, supersaturation occurs from the very early stage of cooling process and crystallization will start at higher temperature. However, when the die air temperature increased the onset crystallization temperature did not change. This result was expected since onset crystallization temperature is measured as the polymer pervious thermal history is erased.
This analysis is helpful to confirm that degradation does not happen once the air temperature is increased during meltblowing process.

**DCS Heating Thermogram**

Overall crystallinity is evaluated from the modulated DSC heating thermogram. As can be seen in figure 6.2, for both PP control nonwoven and nonwovens containing nucleating agent, crystallinity (%) decreased as the die air temperature increased. This can be attributed to less available driving force for crystallization at higher die air temperature. However, the overall crystallinity of nonwovens containing nucleating agent are higher compared to PP control nonwovens due to more nucleation sites available for the crystallization in presence of nucleating agent.

![Crystallinity (%) vs Die Air Temperature](image)

**Figure 6.2** : Crystallinity (%) of PP meltblown nonwovens and PP meltblown nonwovens containing Irgaclear XT 386 at different die air temperatures

135
6.4.1.2 Crystalline Structure

Application of nucleating agent can lead to alteration in crystallization kinetic, fiber and nonwoven formation during meltblowing process. Consequently, nonwovens with different microstructure will be fashioned. Moreover, change of meltblowing die air temperature can lead to change of developed nonwovens crystalline structure. Nonwovens crystalline morphology changes are monitored via WAXD.

![Figure 6.3: X-ray diffractogram of a) PP meltblown nonwoven and b) PP meltblown nonwoven containing Irgaclear XT 386 at different die air temperatures](image)

WAXD patterns of PP meltblown nonwoven containing 0, 0.02 wt. % concentration of nucleating agent at different die air temperatures are shown in figure 6.3.
According to the X-ray diffractogram, for PP meltblown nonwoven (see figure 6.3 a) shape of crystalline peaks slightly changed and became sharper when the die air temperature increased. These crystalline peaks are correspondent to α crystalline form of isotactic polypropylene. Also according to table 6.3, crystals sizes increased (e.g. from 176 to 180 Å) as the die air temperature increased from 255 to 275 °C. Increase of crystals sizes might be because of the lower available driving force for crystallization and formation of less number of nuclei at higher die air temperature.

For PP meltblown nonwoven containing nucleating agent (see figure 6.3 b), crystalline peaks are also correspondent to α crystalline form of isotactic PP which became sharper as the die air temperature increased from 255 to 275 °C. Moreover, according to table 6.3, crystals sizes increased (e.g. from 173 to 178 Å) when the die air temperature increased from 255 to 275 °C.

**Table 6.3**: Crystallite size of PP and PP meltblown nonwoven containing Iragclear XT 386 at different die air temperatures

<table>
<thead>
<tr>
<th>Nucleating agent conc. wt. %</th>
<th>Temperature (°C)</th>
<th>2θ (degree)</th>
<th>FWHM (radian)</th>
<th>Crystal size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>255</td>
<td>19.16</td>
<td>0.429</td>
<td>176</td>
</tr>
<tr>
<td>0.02</td>
<td>255</td>
<td>18.6</td>
<td>0.465</td>
<td>173</td>
</tr>
<tr>
<td>0.02</td>
<td>265</td>
<td>18.5</td>
<td>0.444</td>
<td>175</td>
</tr>
<tr>
<td>0.02</td>
<td>275</td>
<td>19.33</td>
<td>0.422</td>
<td>178</td>
</tr>
</tbody>
</table>
As can be compared in figure 6.3, crystalline peaks of nonwovens containing 0.02 wt. % concentration of Irgaclear XT 386 are sharper compared to control PP meltblown nonwoven, which suggests formation of well-shaped crystals in presence of nucleating agent.

Also for all different die air temperatures, crystals sizes of nonwoven containing Irgaclear XT 386 are slightly smaller compared to the control PP meltblown nonwovens. This can be due to creation of more nucleation sites for crystallization and therefore formation of smaller well-shaped crystals in presence of nucleating agent.

6.4.1.3 Web Properties

Effect of both nucleating agent as the material variable and die air temperature as the process variable on meltblown webs structure and properties have been investigated. As it was explained in DSC analysis study, with addition of nucleating agent in melt blowing process onset crystallization temperature of polymer increased. It can be hypothesized that, increase of onset crystallization temperature of polymer in presence of nucleating agent may lead to faster solidification of polymer melt closer to the meltblowing die face and formation of bulkier structure nonwovens with higher air permeability and lower solidity. Moreover, as it is known when the die air temperature increases in meltblowing of normal PP, solidification of polymer melt may happen slower and lead to formation of tackier fibers and webs with higher solidity. However, it is necessary to understand the effect die air temperature changes in meltblowing of polymer containing nucleating agent (Irgaclear XT 386).

As can be seen in figure 6.4 with addition of nucleating agent solidity of nonwovens increased and according to figure 6.5 air permeability of them increased. These results support the hypothesis that by application of Irgaclear XT 386 in melt blowing process,
solidification of polymer melt can happen faster and lead to formation of bulkier structure nonwovens with lower solidity and higher air permeability.

Moreover, according to figure 6.4, solidity of both PP nonowovens and samples containing Irgaclear XT 386 increased as the die air temperature increased while according to the figure 6.5 air permeability of these samples decreased. This can be attributed to slower solidification and lower viscosity of polymer melt at higher die air temperature therefore formation of webs with higher solidity and lower air permeability.

![Figure 6.4: Effect of Irgaclear XT 386 and change of die air temperature on solidity of meltblown nonwovens](image-url)
Figure 6.5: Effect of Irgaclear XT 386 and change of die air temperature on air permeability of meltblown nonwovens

According to SEM images shown in figure 6.6 (a, b) and figure 6.7, for both PP meltblown nonwovens and PP nonwovens containing Irgaclear XT 386 mean fiber diameter did not changed significantly as the die air temp increased. However, for nonwovens containing nucleating agent mean fiber diameters slightly increased due to faster solidification of polymer melt closer to the meltblowing die face in presence of nucleating agent.
Figure 6.6: a) Fibers in PP meltblown nonwoven, b) Fibers in PP meltblown nonwoven containing 0.02 wt. % concentration of Irgaclear XT 386

Figure 6.7: Fiber diameter in meltblown nonwovens at different die air temperatures
6.4.2 Effect of Die to Collector Distance (DCD) on PP Meltblown Webs Containing Irgacleara XT 386

6.4.2.1 Differential Scanning Calorimeter (DSC) Analysis

DSC Cooling Thermogram

Thermal transition temperature for cooling thermogram of crystallization is affected by presence of nucleating agent in polymer. The cooling graph indicates that as the Irgaclear XT 386 concentration increases to 0.02 wt. %, onset crystallization temperature increased by 10 °C to its maximum value 131 °C (see figure 6.8).

![DSC Cooling Thermogram](image_url)

**Figure 6.8**: DSC cooling thermogram of PP nonwovens and PP nonwovens containing Irgaclear XT 386 at different DCDs (crystallization exotherm)
In fact, by application of nucleating agent and presence of more nuclei in polymer melt, supersaturation occurs from the very early stage of cooling process and crystallization will start at higher temperature. However, as the DCD increased the onset crystallization temperature did not change. This result was expected since onset crystallization is measured as the polymer pervious thermal history is erased.

**DCS Heating Thermogram**

Overall crystallinity is evaluated from the modulated DSC heating thermogram. As can be seen in figure 6.9, for PP control nonwoven crystallinity % increased from 20 to 22 % as the DCD increased from 150 to 350 cm. On the other hand, for webs containing nucleating agent, crystallinity % increased from 21 to 26 % when the DCD increased from 150 to 350 cm. As it is explained, crystallinity % of both PP control meltblown nonwoven and the web containing nucleating agent increased when the DCD increased. The increase of crystallinity % can be attributed to longer cooling time and higher chance of crystallization before reaching the collector at higher DCD. However, overall crystallinity of nonwovens containing nucleating agent are higher compared to PP control nonwoven at all different DCDs which can be due to creation of more nuclei and faster crystallization rate in presence of nucleating agent. The highest obtained degree of crystallinity was 26 % for nonwoven containing nucleating agent at DCD of 350 cm.
Figure 6.9: Crystallinity (%) of PP meltblown nonwoven and PP meltblown nonwoven containing Irgaclear XT 386 at different DCDs

6.4.2.2 Crystalline Structure

Application of nucleating agent can lead to alteration in crystallization kinetic, fiber and nonwoven formation during meltblowing process. Consequently, nonwovens with different microstructure will be fashioned. Moreover, change of meltblowing DCD can lead to change of developed nonwovens crystalline structure. Nonwovens crystalline morphology changes are monitored via WAXD.
WAXD patterns of PP meltblown nonwoven containing 0, 0.02 wt. % concentration of nucleating agent at different DCDs are shown in figure 6.10. According to the X-ray diffractogram, for PP meltblown nonwoven (see figure 6.10 a and table 6.4) crystals sizes decreased (e.g. from 176 to 100 Å) as the DCD increased from 150 to 350 cm. The decrease of crystals sizes might be because of the longer cooling time and more available driving force for crystallization at higher DCD. In fact chance of crystallization before reaching the collector is increased at higher DCD. For PP meltblown nonwoven containing nucleating agent (see figure 6.10 b, table 6.4), crystals sizes decreased (e.g. from 173 to 100 Å) when the DCD increased from 150 to 350 cm.

As can be compared in figure 6.10, for all different DCDs, crystals sizes of nonwoven containing Irgaclear XT 386 are slightly smaller compared to the control PP meltblown
nonwovens. This can be attributed to creation of more nucleation sites for crystallization and therefore formation of smaller crystals in presence of nucleating agent.

Table 6.4: Crystallite size of PP and PP meltblown nonwoven containing Iragclear XT 386 at different DCDs

<table>
<thead>
<tr>
<th>Nucleating agent conc. wt. %</th>
<th>DCD (mm)</th>
<th>2θ (degree)</th>
<th>FWHM (radian)</th>
<th>Crystal size (Å⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-150</td>
<td></td>
<td>19.16</td>
<td>0.429</td>
<td>176</td>
</tr>
<tr>
<td>0-250</td>
<td></td>
<td>18.76</td>
<td>0.484</td>
<td>166</td>
</tr>
<tr>
<td>0-350</td>
<td></td>
<td>18.90</td>
<td>0.800</td>
<td>101</td>
</tr>
<tr>
<td>0.02-150</td>
<td></td>
<td>18.6</td>
<td>0.465</td>
<td>173</td>
</tr>
<tr>
<td>0.02-250</td>
<td></td>
<td>18.66</td>
<td>0.492</td>
<td>163</td>
</tr>
<tr>
<td>0.02-350</td>
<td></td>
<td>18.56</td>
<td>0.803</td>
<td>100</td>
</tr>
</tbody>
</table>

6.4.2.3 Web Properties

Effect of both nucleating agent as the material variable and die air temperature as the process variable on meltblown webs structure and properties have been investigated. As it was explained according to DSC analysis, with addition of nucleating agent in melt blowing process onset crystallization temperature of polymer increased. It can be hypothesized that, increase of onset crystallization temperature of polymer in presence of nucleating agent may lead to faster solidification of polymer melt closer to the meltblowing die face and formation of bulkier structure nonwovens with higher air permeability and lower solidity.

Moreover, as it is known when the DCD increases in meltblowing of normal PP, chance of crystallization before reaching the collector increases which can lead to formation of
less tacky fibers and loftier webs with higher air permeability and lower solidity. However, it is necessary to understand the effect of DCD changes in meltblowing of polymer containing nucleating agent.

As can be seen in figure 6.11, with addition of nucleating agent solidity of nonwovens increased and according to figure 6.5, air permeability of samples increased. These results support the hypothesis that by application of Irgaclear XT 386 in meltblowing process, solidification of polymer melt can happen faster and lead to formation of bulkier structure nonwovens with lower solidity and higher air permeability.

Moreover, according to figure 6.11, solidity of both PP nonwovens and samples containing Irgaclear XT 386 decreased as the DCD increased while according to the figure 6.12, air permeability of these samples increased. This can be attributed to higher chance of polymer melt crystallization before reaching the collector which can lead to formation of less tacky fibers so loftier webs with higher air permeability and lower solidity. According to SEM images shown in figure 6.13 (a,b) and figure 6.14, for both PP meltblown nonwovens and webs containing Irgaclear XT 386, mean fiber diameters did not change significantly as the die air temperature increased. However, for nonwovens containing nucleating agent mean fiber diameters slightly increased due to the faster solidification of polymer melt closer to the meltblowing die face in presence of nucleating agent.
Figure 6.11: Effect of Irgaclear XT 386 and change of DCD on solidity of meltblown nonwovens

Figure 6.12: Effect of Irgaclear XT 386 and change of DCD on air permeability of meltblown nonwovens
Figure 6.13: a) Fibers in PP meltblown nonwoven, b) Fibers in PP meltblown nonwoven containing Irgaclear XT 386

Figure 6.14: Fiber diameter of meltblown nonwovens at different DCDs
6.5 Conclusion

In this research structure-property-processing relationship of meltblown nonwovens containing Irgaclear XT 386 nucleating agent was investigated. Therefore, nucleating agent was used as the material variable while DCD and die air temperature were chosen as the meltblowing process variables. Results indicate that, by application of the Irgaclear XT 386 in meltblowing process onset crystallization temperature of polymer increased which led to faster solidification of polymer melt and formation of bulkier structure nonwovens with lower solidity and higher air permeability. Moreover, increase of die air temperature in meltblowing of polymer containing nucleating agent led to change of crystalline structure, lower crystallinity %, higher solidity and lower air permeability of web. Furthermore, increase of DCD resulted in higher crystallinity %, slightly smaller crystals sizes, higher air permeability and lower solidity of nonwovens containing nucleating agent.
6.6 References


7. Overall Conclusions and Recommendations for Future Work

7.1 Overall Conclusion

As it is discussed in introduction part of this dissertation, the overall objective of this research was “Investigate the effect of nucleating agent on morphology and mechanical properties of filaments and performance of resulting nonwovens”. In this regard, polypropylene (PP) and 1,3,5-tris(2,2-dimethylpropionylamino) (Irgaclear XT 386) were used as materials.

In conclusion, application of Irgaclear XT 386 resulted in higher onset crystallization temperature and faster crystallization rate of polymer, higher elongation at break and toughness for the fibers.

On the other hand with addition of Irgaclear XT 386 in meltblowing process, onset crystallization temperature of polymer increased which led to faster solidification of polymer melt and formation of bulkier structure nonwovens with higher air permeability and improved filtration properties.

Moreover, increase of Die to Collector Distance (DCD) in meltblowing of polymer resulted in decrease of crystal size, increase of crystallinity %, higher air permeability and lower solidity of webs, while these effects are accelerated in presence of nucleating agent.

Moreover, increase of die air temperature led to change of crystalline structure, decrease of crystallinity %, lower air permeability and higher solidity of meltblown nonwovens, while these effects are decelerated in presence of nucleating agent.
7.2 Recommendation for future

In this research the effect of one type of nucleating agent 1,3,5-tris(2,2-dimethylpropionylamino) (commercially known as Irgaclear XT 386) on morphology and properties of PP fibers and meltblown nonwovens has been investigated. Hot stage optical microscopy technique can be used to monitor the crystallization process. Also, it is recommended to investigate the effect of other types of nucleating agent and polymer on morphology and properties of nonwovens.

During the course of this study, influence of nucleating agent on meltblown nonwovens has been investigated. It is recommended to understand the effect of Irgaclear XT 386 nucleating agent on bonding and structure-properties of developed nonwovens through spunbonding process.

Moreover, to understand the structure property processing relationship of meltblown nonwovens containing Irgaclear XT 386, DCD and die air temperature were considered as the meltblowing process variables. In fact, change of each of these variables along with the presence of nucleating agent can affect crystallization and therefore properties of the developed webs. However, studying the effect of other processing parameters including polymer throughput, air flow and melt temperature would be interesting to explore.