

ห้องสมุดงานวิจัย สำนักงานคณะกรรมการการวิจัยแห่งชาติ



E47347

**EFFECT OF SORBITOL DERIVATIVES ON MECHANICAL
PROPERTIES AND MORPHOLOGY OF
POLYPROPYLENE FIBER**

THANITA SUTTHATANG

**A Thesis Submitted to the Graduate School of Naresuan University
in Partial Fulfillment of the Requirements
for the Master of Science Degree
in Industrial Chemistry**

May 2012

Copyright 2012 by Naresuan University



E47347

**EFFECT OF SORBITOL DERIVATIVES ON MECHANICAL
PROPERTIES AND MORPHOLOGY OF
POLYPROPYLENE FIBER**

THANITA SUTTHATANG



**A Thesis Submitted to the Graduate School of Naresuan University
in Partial Fulfillment of the Requirements
for the Master of Science Degree
in Industrial Chemistry
May 2012
Copyright 2012 by Naresuan University**

This thesis entitled "Effect of sorbitol derivatives on mechanical properties and morphology of polypropylene fiber" submitted by Thanita Sutthatang in partial fulfillment of the requirements for the Master of Science Degree in Industrial Chemistry is hereby approved.

C.W. Phetphaisit
.....Chair
(Assistant Professor Chor. Wayakron Phetphaisit, Ph.D.)

Uthai Wichai
.....Committee
(Uthai Wichai, Ph.D.)

Supatra Wangsoub
.....Committee
(Supatra Wangsoub, Ph.D.)

T. Amornsakchai
.....Committee
(Associate Professor Taweechai Amornsakchai, Ph.D.)

Approved

K. Papatwibul
.....
(Assistant Professor Kanungnit Papatwibul, Ph.D.)

Dean of the Graduate School

11 May 2012

Title	EFFECT OF SORBITOL DERIVATIVES ON MECHANICAL PROPERTIES AND MORPHOLOGY OF POLYPROPYLENE FIBER
Author	Thanita Sutthatang
Advisor	Uthai Wichai, Ph.D.
Co-Advisor	Supatra Wangsoub, Ph.D.
Academic Paper	Thesis M.S. in Industrial Chemistry, Naresuan University, 2011
Keywords	Sorbitol derivatives, Polypropylene, Fibril morphology

ABSTRACT

E47347

We here report the chloro and bromo derivatives were used as a nucleating agent for polypropylene. Furthermore, sorbitol derivatives can self-organize to form fibrils in nanometers. SEM and TEM micrographs of gel extracted from organic solvent revealed the fibril network of chloro and bromo derivatives which can be observed their diameter in the range 7-216 nm and length higher than 9 μm . Small amount of these materials was blended with isotactic polypropylene (iPP) by two roll mill machine and the mixture was made to fiber form by extrusion. The effect of halogenated sorbitol derivatives on the crystallization of iPP were studied using different scanning calorimeter technique. It was found that addition of small amount of sorbitol derivative increase the crystallization temperature of iPP to 18 $^{\circ}\text{C}$ compared to neat iPP. No further increase in the crystallization temperature when the amount of additive reach 0.5 wt% for para chloro derivatives. The high level of preferred orientation of iPP lamellar is clearly seen when the samples were dispersed with small amount of sorbitol derivatives under high screw speed. The SEM micrographs of cross section of as-spun iPP fiber were indicated the location of sorbitol derivatives fibrils which aligned within iPP melt. The effect of sorbitol derivatives on mechanical properties of as-spun and drawn iPP fiber were studied by using tensile tester. For as-spun fiber, the effect of amount, substitution position, and type of sorbitol derivatives on mechanical properties of iPP fiber were demonstrated. It was found that the elastic modulus of neat iPP can be increased up to 48 % when 1% wt of *p*-Cl-DBS added. For drawn iPP fiber, the tensile strength and elastic modulus of both amount of sorbitol

E47347

derivatives (0.5 and 1 % wt) fiber increase with draw ratio increase. While the percentage of elongation of fiber decrease with draw ratio increase.

LIST OF CONTENTS

Chapter	Page
I INTRODUCTION.....	1
Rationale for the study.....	1
Aim of this study.....	6
Scope of the study.....	7
II LITERATURE REVIEWS.....	8
Conventional nucleating agents.....	8
Polypropylene.....	10
Dibenzylidene sorbitol (DBS).....	14
III RESEARCH METHODOLOGY.....	32
Materials.....	32
Instruments.....	34
Synthesis of sorbitol derivatives.....	35
Characterization of sorbitol derivatives.....	36
Preparation of polypropylene blend with sorbitol derivatives.....	38
Investigation the effect of sorbitol derivatives on crystallization and melting temperature of iPP by DSC technique.....	38
Fiber preparation.....	39
Mechanical testing.....	40
Characterization of as-spun and drawn fibers.....	40
Flow charts of experiment.....	43

LIST OF CONTENTS (CONT.)

Chapter	Page
IV RESULTS AND DISCUSSION	44
Synthesis of sorbitol derivatives and characterization of sorbitol derivatives.....	44
Gel formation and fibril morphology.....	58
The effect of sorbitol derivatives on crystallization, melting temperature, degree of crystallinity and nucleation of polypropylene.....	65
The effect of sorbitol derivatives on the morphology and orientation of polypropylene.....	78
The Effect of sorbitol derivatives on mechanical properties of polypropylene fiber.....	95
V CONCLUSIONS	111
REFERENCES	113
BIOGRAPHY	122

LIST OF TABLES

Table	Page
1 Chemical and suppliers.....	32
2 Instruments, manufacturers and models.....	34
3 Extrusion condition for sample preparation of neat iPP and iPP/sorbitol derivatives fiber.....	39
4 The percentage of yield of sorbitol derivatives.....	46
5 Melting temperature of sorbitol derivatives by melting apparatus and DSC technique.....	47
6 Functional group annotation of D-sorbitol and 4-chlorobenzaldehyde.....	48
7 Functional group annotation of <i>o</i> -Cl-DBS, <i>m</i> -Cl-DBS, <i>p</i> -Cl-DBS and <i>p</i> - Br-DBS.....	50
8 Chemical shift of reactant (use DMSO-D ₆ as a solvent).....	52
9 Chemical shift of sorbitol derivatives (use DMSO-D ₆ as a solvent).....	54
10 Chemical shift of <i>p</i> -Cl-DBS.....	56
11 Diameter and length of sorbitol derivatives were observed by SEM technique.....	62
12 Diameter of sorbitol derivatives were observed by TEM technique.....	62
13 Crystallization temperature of neat iPP and iPP containing 0.5 %wt of sorbitol derivaitves.....	66
14 Degree of crystallinity of neat iPP and iPP containing 0.5% wt of sorbitol derivatives.....	72
15 Degree of crystallinity of neat iPP and iPP containing different concentration of <i>p</i> -Cl-DBS.....	72
16 Degree of crystallinity of as-spun neat iPP fiber and as-spun iPP containing different concentration of <i>p</i> -Cl-DBS fiber.....	73

LIST OF TABLES (CONT.)

Table	Page
17 q- and d-space of iPP as-spun fiber at different die temperature at screw speed 2 rpm.....	81
18 q- and d-space of iPP as-spun fiber with small amount of sorbitol derivatives at different die temperatures at screw speed 2 rpm.....	86
19 Diameter of sorbitol derivatives fibril and extrude iPP fiber+1% sorbitol derivatives.....	94
20 Mechanical properties of as spun neat iPP fiber and as spun iPP containing different concentrations of <i>p</i> -Cl-DBS fiber.....	96
21 Mechanical properties for neat iPP fiber and iPP fiber containing 0.5 % wt of sorbitol derivatives.....	99
22 Mechanical properties for neat iPP fiber and iPP fiber containing 0.5 % wt of sorbitol derivatives at different draw ratio.....	108
23 Mechanical properties for neat iPP fiber and iPP fiber containing 1 % wt of sorbitol derivatives at different draw ratio.....	109

LIST OF FIGURES

Figures	Page
1 Chemical structure of 1,3:2,4-dibenzylidene sorbitol (DBS).....	3
2 Schematic mechanism for the role of HDPE molecular weight on shear-induced shish-kebab structure in LLDPE/HDPE blend: (a) high molecular weight and (b) low molecular weight.....	5
3 Schematic illustration of the stereochemical configuration of PP. A) isotactic PP, B) syndiotactic PP, and C) atactic PP.....	11
4 X-ray diffraction patterns of different iPP crystal forms.....	13
5 Chemical structure of asymmetric alditol diacetal.....	16
6 Chemical structure of 1,3:2,4-dibenzylidene sorbitol (DBS) illustrating the unique “butterfly” shape of the molecule.....	17
7 Illustration of the impact of the nature of the solvent on the clarity of DBS gel, (from left to right: butyl adipate, methylphthalate, butylphthalate, hexane).....	18
8 Electron micrographs of xerogel fibers of DBS, the gel preparation on the microscope grid from a tetrahydrofuran solution, later gelled by addition of benzene.....	18
9 TEM images of PEG/DBS organogel.....	19
10 Chemical structure of 1,3:2,4-di-p-methylbenzylidene sorbitol (MDBS).....	21
11 Effect of DBS on the crystallization temperature of iPP.....	22
12 Concentration dependency of DBS on crystallization temperature of iPP.....	23
13 Optical properties of iPP/DMDBS for different amounts of DMDBS. Illustrates viewed through injection molded plaques containing 0.1, 0.5, 2, and 10 % wt of DMDBS (top) and measured values for haze (▲) and clarity (■) as a function of the DMDBS content (bottom).....	24

LIST OF FIGURES (CONT.)

Figures	Page
<p>14 Optical micrographs of the morphology of compression molded film of binary i-PP/DMDBS mixtures containing different amounts of DMDBS (in wt %): (a) 0.1, (b) 0.2, (c) 40.0. Scale bar 100 μm....</p>	25
<p>15 (a) Stress-strain curves measured for fibers fabricated using TP2 with low SDR, where the solid black, the gray, and dashed lines were taken for 0, 1 and 0.4% DMDBS, respectively. (b) Stress-strain curves measured for fibers, containing 0.4% MDDBS, fabricated using TP2, where the black and gray lines indicate, low and high SDR, respectively.....</p>	27
<p>16 Templating the orientation through crystallization. WAXS patterns showing the effect of the DBS on the crystal orientation distribution of the semi-crystalline polymers. (a) and (c) are the non-modified CPP and PE. (b) and (d) are the DBS-modified CPP add PE. In (d) the inset shows the SAXS pattern for the same sample.....</p>	29
<p>17 Plots showing wide angle X-ray scattering intensity as a function of q for the system under investigation. The label to the right of each trace indicate the percentage DBS.....</p>	30

LIST OF FIGURES (CONT.)

Figures	Page
18 WAXS and SAXS patterns obtained for samples of PCL and 3 % DBS/PCL samples at the same point of the thermal and shear flow cycle. Each set of pattern is organized as a square block of four, representing WAXS and SAXS, during shear in the melt, and WAXS and SAXS at room temperature after crystallization. (a), (b), (e) and (f)-PCL with no shear; (c), (d), (g) and (h)-PCL with shear; (i), (j), (m) and (n)-DBS/PCL with no shear; (k), (l), (o) and (p)-DBS/PCL with shear. The flow direction is vertical.....	31
19 Synthesis of sorbitol derivatives (DBS).....	35
20 The equipment used in the synthesis.....	36
21 Schematic of mini-extruder and fiber line diagram.....	39
22 Schematic representation of fiber surface preparation for etching, a) cross section fiber and b) longitudinal section fiber.....	41
23 Experiment overview.....	43
24 Synthesis of various sorbitol derivatives.....	45
25 FT-IR spectra of D-sorbitol (upper) and 4-chlorobenzaldehyde (lower).....	48
26 FT-IR spectra of sorbitol derivatives.....	49
27 ¹ H NMR spectra of A) D-sorbitol and B) 4-chlorobenzaldehyde.....	52
28 ¹ H NMR spectra of sorbitol derivatives.....	54
29 ¹³ C NMR spectrum of <i>p</i> -Cl-DBS.....	57
30 SEM micrographs of sorbitol derivatives in different concentration and solvents.....	60
31 TEM micrographs of sorbitol derivatives in different concentrations and solvents.....	62

LIST OF FIGURES (CONT.)

Figures	Page
32 Cooling thermograms of neat iPP and iPP containing 0.1 % wt of sorbitol derivatives by solution blending.....	66
33 Crystallization temperature of neat iPP and iPP containing 0.1%wt of sorbitol derivatives by solution blending.....	66
34 Crystallization temperature of neat iPP and iPP containing different concentrations of <i>p</i> -Cl-DBS by solution blending.....	67
35 Cooling thermograms of neat iPP and iPP containing 0.5 %wt of sorbitol derivatives by two-roll mill.....	68
36 Crystallization temperature of neat iPP and iPP containing 0.5%wt of sorbitol derivatives by two-roll mill.....	69
37 Cooling thermograms of neat iPP and iPP containing different concentrations of <i>p</i> -Cl-DBS by two-roll mill.....	70
38 Crystallization temperature of neat iPP and iPP containing different concentrations of <i>p</i> -Cl-DBS by two-roll mill.....	70
39 Melting thermograms of neat iPP and iPP containing different concentrations of <i>p</i> -Cl-DBS.....	71
40 Melting temperature of neat iPP and iPP containing different concentrations of <i>p</i> -Cl-DBS.....	72
41 Melting temperature of neat iPP and iPP containing 1% wt of sorbitol derivatives.....	73
42 Optical micrographs of a) neat iPP b) iPP/0.1% <i>o</i> -Cl-DBS c) iPP/0.1% <i>m</i> -Cl-DBS d) iPP 0.1% <i>p</i> -Cl-DBS and e) iPP/0.1% <i>p</i> -Br-DBS from melt-blend.....	76
43 Optical micrographs of iPP containing 0.5% wt of a) <i>o</i> -Cl-DBS, b) <i>m</i> -Cl-DBS, c) <i>p</i> -Cl-DBS and d) <i>p</i> -Br-DBS from melt-blend.....	77

LIST OF FIGURES (CONT.)

Figures	Page
44 SAXS and WAXS patterns of neat iPP fiber at different die temperatures screw speed 2 rpm.....	79
45 Equatorial section of WAXS patterns of neat iPP at different die temperatures.....	80
46 SAXS patterns of as-spun iPP fiber containing 0.5 % wt of sorbitol derivatives at different die temperatures, and WAXS patterns of as-spun iPP fiber containing 0.5 % wt of sorbitol derivatives at die temperature 190 °C, screw speed 2 rpm.....	82
47 Equatorial sections of WAXS patterns of neat iPP and PP+0.5% wt of sorbitol derivatives at die temperature 190 °C.....	83
48 Equatorial sections of WAXS patterns of neat iPP and PP+1% wt of sorbitol derivatives at die temperature 225°C.....	84
49 SAXS and WAXS patterns of as-spun iPP fiber containing 1 % wt of sorbitol derivatives at different die temperatures and screw speeds.....	85
50 WAXS patterns of as-spun neat iPP different screw speeds at die temperature 190 °C.....	87
51 I) SAXS and WAXS patterns, II) Equatorial sections of WAXS patterns and III) Meridional section of SAXS of as-spun iPP with 1 % wt of different types of sorbitol derivatives at different screw speeds and die temperatures.....	88
52 WAXS patterns of drawn neat iPP fiber at different die temperature, and iPP fibers containing 1 % wt of sorbitol derivatives at die temperature 190 °C.....	90
53 Equatorial section of drawn iPP fiber at die temperature 225 °C and 190°C with different draw ratios.....	91

LIST OF FIGURES (CONT.)

Figures	Page
54 SEM micrographs of cross section morphology of as-spun neat iPP and as-spun iPP with four different types of sorbitol derivatives after etching with permanganic reagent for 2 hours.....	93
55 Deformation behavior curves of as spun neat iPP fiber and as spun iPP containing different concentrations of <i>p</i> -Cl-DBS fiber.....	92
56 Tensile strength of iPP fiber containing different concentrations of <i>p</i> -Cl-DBS.....	97
57 Elastic modulus of iPP fiber containing different concentrations of <i>p</i> -Cl-DBS.....	97
58 Percentage of elongation of iPP fiber containing different concentrations of <i>p</i> -Cl-DBS.....	98
59 Tensile strength of as spun neat iPP and as spun iPP fiber containing 0.5 % wt of sorbitol derivatives.....	99
60 Elastic modulus of as spun neat iPP and as spun iPP fiber containing 0.5 % wt of sorbitol derivatives.....	100
61 Percentage of elongation of as spun neat iPP and as spun iPP fiber containing 0.5 % wt of sorbitol derivatives.....	100
62 Tensile strength of as spun neat iPP and as spun iPP fiber containing 1 % wt of sorbitol derivatives.....	101
63 Elastic modulus of as spun neat iPP and as spun iPP fiber containing 1 % wt of sorbitol derivatives.....	102
64 Percentage of elongation of as spun neat iPP and as spun iPP fiber containing 1 % wt of sorbitol derivatives.....	102
65 Tensile strength of drawn neat iPP fiber and drawn iPP fiber containing 0.5 % wt of sorbitol derivatives at different draw ratios.....	103

LIST OF FIGURES (CONT.)

Figures	Page
66 Elastic modulus of drawn neat iPP fiber and drawn iPP fiber containing 0.5 % wt of sorbitol derivatives at different draw ratios.....	104
67 Percentage of elongation of drawn neat iPP fiber and drawn iPP fiber containing 0.5 % wt of sorbitol derivatives at different draw ratios.....	105
68 Tensile strength of drawn neat iPP fiber and drawn iPP fiber containing 1 % wt of sorbitol derivatives at different draw ratios.....	106
69 Elastic modulus of drawn neat iPP fiber and drawn iPP fiber containing 1 % wt of sorbitol derivatives at different draw ratios....	107
70 Percentage of elongation of drawn neat iPP fiber and drawn iPP fiber containing 0.5 % wt of sorbitol derivatives at different draw ratios.....	107