STUDY ON CRYSTALLIZATION KINETICS AND SUBSEQUENT MELTING BEHAVIOR OF POLYMERS WITH DIFFERENT MOLECULAR CHARACTERISTICS AND POLYMERS FILLED WITH VARIOUS TYPES OF ADDITIVES

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ABSTRACT

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Crystallization and subsequent melting behavior for six syndiotactic polypropylene (sPP) resins having different molecular characteristics, medium-density polyethylene (MDPE) filled with 3 types of pigments (i.e. diarylide, phthalocyanine, and quinacridone), and isotactic polypropylene (iPP) filled with titanium(IV)oxide (TiO_2) with 3 different surface modifications were investigated by differential scanning calorimetry (DSC). The crystallization kinetics were analyzed based on various macrokinetic models, i.e. Avrami, Malkin, Urbanovici-Segal, Ozawa, and Ziabicki. The equilibrium melting temperature (T_m^0) was also estimated based on the linear and non-linear Hoffman-Weeks extrapolative methods. In general, the estimated T_m^0 values were found to increase with increasing syndiotacticity level. By comparing these values along with the values obtained from literature, the T_m^0 value for a perfect sPP can be estimated. The subsequent melting behavior of sPP after crystallization process exhibited either a single melting endotherm or double melting endotherms. For the crystallization behavior of pigmented MDPE resins, it was found that diarylide could be the only pigment that was effective in accelerating the crystallization processes compared to other two pigments.

บทคัดย่อ

ภคิน ถนอมเกียรติ : การศึกษาพฤติกรรมการตกผลึกและการหลอมเหลวของผลึกที่เกิดขึ้นของพอลิเมอร์ที่มีคุณลักษณะของโมเลกุลต่างกัน และพอลิเมอร์ที่มีการใส่สารเติมชนิดต่าง ๆ (Study on Crystallization Kinetics and Subsequent Melting Behavior of Polymers with Different Molecular Characteristics and Polymer Filled with Various Types of Additives) อ. ที่ปรึกษา : รศ. ดร. พิชญ์ ศุภผล และ ศ.สตีเฟน เชง 159 หน้า

พฤติกรรมการตกผลึกและการหลอมเหลว ของซินดิโอแทคติกพอลิโพรพิลีน ที่มีคุณลักษณะของโมเลกุลต่าง ๆ กัน พอลิเอทิลีนความหนาแน่นปานกลางที่เติมด้วยรงควัตถุต่างกันสามชนิด (ได้แก่ ไดอะริลไลด์ ฟะทาโลไซยานิน และควินอะคริโดน) และไอโซแทคติกพอลิโพรพิลีน ที่เติมด้วยไทเทเนียมไดออกไซด์ที่มีอนุภาคขนาดนาโนเมตร และมีคุณสมบัติของพื้นผิวต่างกันสามชนิด ได้รับการศึกษาโดยอาศัยเทคนิคดิฟเฟอเรนเชียล สแกนนิง แคลอรีเมทรี ซึ่งสามารถนำผลการทดลองจากเทคนิคดังกล่าวมาวิเคราะห์ โดยอาศัยโมเดลต่าง ๆ ได้แก่ อาฟรามี มาลคิน เออร์บาโนวิช-เซกาล โอซาวา และ ไซอะบิกกิ ซึ่งสามารถทำให้สามารถเปรียบเทียบอัตราการตกผลึก รวมทั้งกลไกการตกผลึกของพอลิเมอร์ต่าง ๆ ดังกล่าวได้ จุดหลอมเหลวสมดุลของพอลิเมอร์สามารถหาได้จากวิธีการของฮอฟแมน-วีค ซึ่งพบว่า เมื่อปริมาณซินดิโอแทคติกมากขึ้น ค่าจุดหลอมเหลวสมดุลจะมีค่าเพิ่มขึ้น นอกจากนี้ ยังทำให้ประมาณค่าของจุดหลอมเหลวสมดุลสำหรับซินดิโอแทคติกพอลิโพรพิลีนที่มีปริมาณซินดิโอแทคติกร้อยเปอร์เซ็นต์ได้ สำหรับรงควัตถุที่มีผลต่อการตกผลึกของพอลิเอทีลีนนั้น พบว่า สารไดอะริลไลด์ เป็นสารที่สามารถเร่งการตกผลึกของพอลิเอทิลีนได้ดีที่สุด ในส่วนของการตกผลึกของไอโซแทคติกพอลิโพรพิลีน ที่เติมด้วย ไทเทเนียมไดออกไซด์ที่มีอนุภาคขนาดนาโนเมตร พบว่า ไททาเนียมไดออกไซด์ ที่ฉาบพื้นผิวด้วยซิลิกอนไดออกไซด์ จะสามารถช่วยให้เกิดการตกผลึกของพอลิโพรพิลีนได้ดีกว่า ไททาเนียมไดออกไซด์ที่ไม่ได้ผ่านการฉาบสารเคลือบผิว แต่ไททาเนียมไดออกไซด์ที่ฉาบด้วยกรดไขมัน มีแนวโน้มในการทำให้กระบวนการตกผลึกของพอลิโพรพิลีนช้าลง

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ABBREVIATIONS

sPP	syndiotactic polypropylene
iPP	isotactic polypropylene
MDPE	medium-density polyethylene
DSC	different scanning calorimetry
NMR	nuclear magnetic resonance
LHW	linear Hoffman-Weeks extrapolation method
NLHW	non-linear Hoffman-Weeks extrapolation method
PY	pigment yellow (diarylide C.I.21108)
PB	pigment blue (phthalocyanine C.I.74160)
PR	pigment red (quinacridone C.I.73915)

LIST OF SYMBOLS

t	time
T	temperature
T_c	crystallization temperature
T_m	melting temperature
T_m^0	equilibrium melting temperature
ΔT_c	degree of undercooling defined as T_m^0 - T_c
$\theta(t)$	relative crystallinity function of time
$\theta(T)$	relative crystallinity function of temperature
dH_c	instantaneous enthalpy of crystallization released at an arbitrary crystallization time
ΔH_c	enthalpy of crystallization released over the course of crystallization period
G	linear growth rate of crystal
I	primary nucleation rate
K_A	Avrami rate constant
n_A	Avrami exponent
C_0	Malkin exponent
C_1	Malkin rate constant
K_{US}	Urbanovici-Segal rate constant
n_{US}	Urbanovici-Segal exponent
r	parameter in Urbanovici-Segal macrokinetics model which satisfies the condition r>0
K_O	Ozawa rate constant
n_O	Ozawa exponent
ϕ	cooling rate
$K(T)$	temperature dependent crystallization rate function
K_{max}	maximum crystallization rate

T_{max}	the temperature which exhibit the maximum crystallization rate
D	the width at the half-height of the crystallization rate function of temperature
G_z	Ziabicki's crystallizability
G_ϕ	crystallizability at an arbitrary cooling rate
$\dot{\theta}_\phi(T)$	derivation function of the relative crystallinity as a function of temperature
$\dot{\theta}_{max,\phi}$	the maximum crystallization rate of the derivation function of the relative crystallinity
D_ϕ	the width at half-height of the derivation function of the relative crystallinity
σ	lateral surface free energy of crystal lamellae
σ_e	fold surface free energy of crystal lamellae
l	crystal lamelar thickness
l_{min}	the minimum lamellar thickness needed to form a thermodynamically stable nucleus
l_g*	critical lamellar thickness to form a thermodynamically stable nucleus at the fastest rate
δl	the increment above l_{min} to give l_g*
k	Boltzman constant
β^m	thickening coefficient
σ_e^{GT}	the basal interfacial free energy associated with nuclei of critical size including the extra lateral surface energy due to fold protrusion and the mixing entropy associated with stems of different lengths
$\sigma_e^!$	the interfacial energy associated with the formation of the basal plane of the initial crystals
ΔH_f^0	the equilibrium enthalpy of fusion
Δt_{inc}	incubation period or time period which the polymer is still in the molten state
Δt_c	crystallization time
T_{onset}	the actual temperature where the sample began to crystallize

t_θ	crystallization time at an arbitrary relative crystallinity
$t_{0.01}$	crystallization time at relative crystallinity equal to 0.01
$t_{0.99}$	crystallization time at relative crystallinity equal to 0.99
$t_{0.5}$	crystallization time at relative crystallinity equal to 0.5 or crystallization half-time
$t_{0.5}^{-1}$	reciprocal crystallization half-time