光學級PET功能性聚酯材料物性及微結構探討

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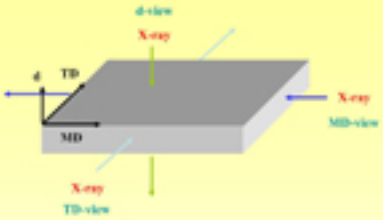
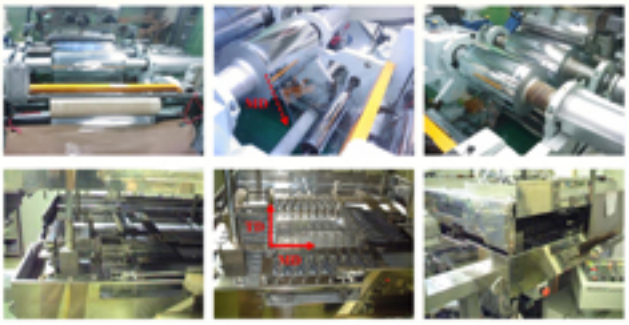


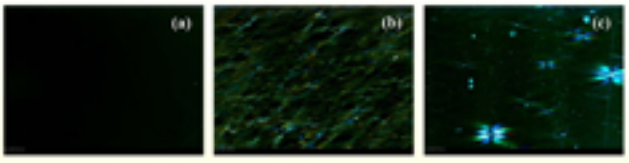
研究重點

雙軸延伸PET(BOPET)膜可作為TFT-LCD中觸控面板ITO膜。此種應用對於膜的透光度、霧度、熱起皺、潔淨度、表面平整度等性質要求的規格門檻極高（稱為「光學級」）。台灣的聚酯產業產線機制完整，每年的產品生產量非常龐大，但所生產之PET酯粒與膜均無法達到光學級應用之門檻。工研院材化所高分子組於2009年積極啟動光學級PET膜技術的開發。研究重點將在PET的分子設計、聚合及改質與雙軸延伸加工技術的改良與控制。由於PET膜的光學特性、熱穩定性及機械強度均與其內部微結構有著密不可分的關係。本研究的目的在於協助高分子組進行PET酯粒及PET膜的微結構深入分析，我們將利用各種分析技術（包括熱分析 (DSC)、偏光顯微鏡 (POM)、穿透式電子顯微鏡 (TEM)、原子力顯微鏡 (AFM)、小角度X光散射 (SAXS)、廣角度X光散射 (WAXS)、小角度光散射 (SALS)、及傅立葉轉換紅外光譜儀 (FTIR)等）去解析高分子組所發展的PET材料在雙軸延伸製程各個步驟中的結構與其演化。包括：晶體順向性與空間排列特徵、微米尺度之特徵超結構、晶體成核密度、晶板厚度與球晶尺寸、非結晶區之分子排列特性、結晶熱力學參數（熔點、結晶度）、及結晶動力學參數（成核速率與晶體成長速率）等。我們希望藉由此研究能建立結構控制的準則，再進一步回饋給分子設計與加工製程之研究人員，瞭解微結構與巨觀膜性質間的關連性，進行進一步之參數調整，以期達到光學級PET膜開發的目的。

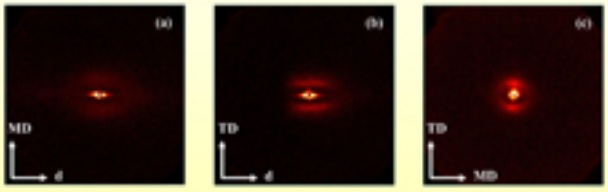
研究成果



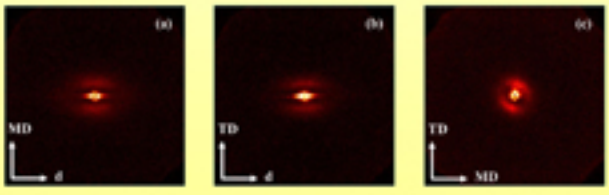
圖一 雙軸延伸製程示意圖。



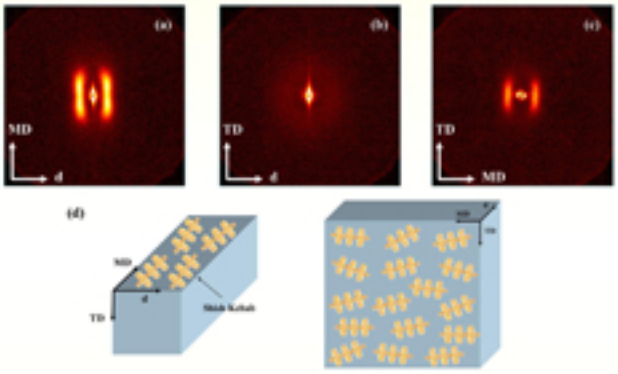
圖二 (a) A公司市售光學膜; (b) B公司市售光學膜; (c) 自製光學膜之偏光特性比較。



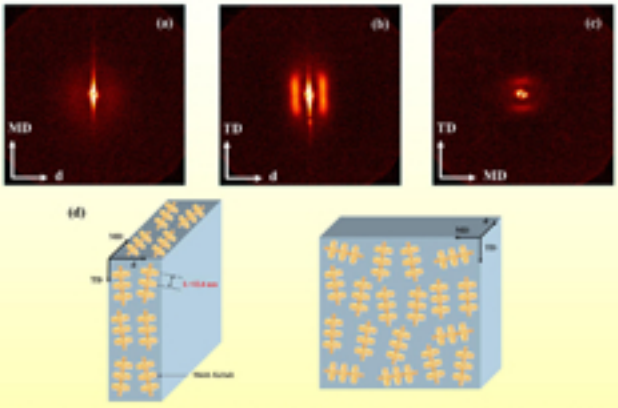
圖三 A公司市售光學膜之2D SAXS圖譜 (a) X-ray沿TD方向入射 (TD-view); (b) X-ray沿MD方向入射 (MD-view); (c) X-ray沿d方向入射 (d-view)。



圖四 B公司市售光學膜之2D SAXS圖譜 (a) X-ray沿TD方向入射 (TD-view); (b) X-ray沿MD方向入射 (MD-view); (c) X-ray沿d方向入射 (d-view)。



圖五 自製光學膜以3 x 1倍率拉伸經熱定型處理後之2D SAXS圖譜 (a) X-ray沿TD方向入射 (TD-view); (b) X-ray沿MD方向入射 (MD-view); (c) X-ray沿d方向入射 (d-view); (d) shish-kebab結構於真實空間中排列之示意圖。



圖六 自製光學膜以3 x 4倍率拉伸經熱定型處理後之2D SAXS圖譜 (a) X-ray沿TD方向入射 (TD-view); (b) X-ray沿MD方向入射 (MD-view); (c) X-ray沿d方向入射 (d-view); (d) shish-kebab結構於真實空間中排列之示意圖。

研究心得

本專案是與工業技術研究院材化所合作，期望能將高分子物理之所學相關知識與實際線上製程結合，瞭解微結構與PET光學膜巨觀性質間的關聯性，以期達到光學級PET膜開發之目的。於該專案的研究成果中，我們成功建立延伸倍率及熱定型溫度與微結構的關聯，相信這些結果對於業界產線的改良勢必有實質上的幫助。本專案是一個成功將高分子學理實際應用在改良業界製程之案例，其成就及意義非凡。雖然在研究過程中，往往會面臨學術理論無法與實際操作匹配之窘境，然而在經過專案的實驗設計及參數調整後，最終仍成功藉由微結構之解析找出影響光學膜最終巨觀性質的關鍵要因。

Orthogonal Crystal Orientation in Double-Crystalline Block Copolymer

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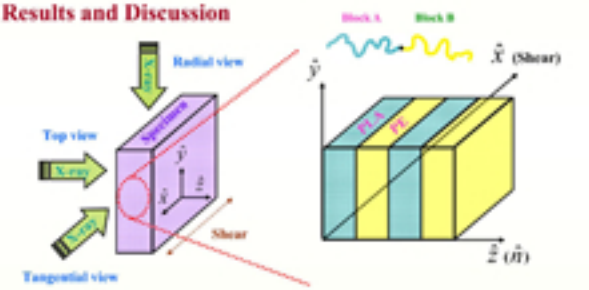
Abstract

Incorporation of crystallization into the self-organization mechanism of block copolymers to generate a hierarchically ordered structure may enrich their property and functionality. For directional control of properties, the manipulation of crystal orientation confined within the nanoscale microdomains is the most important fundamental task. In this study, we explore the orientation of crystals formed within the lamellar domains of a diblock copolymer composing of two crystallizable blocks, i.e., poly(l-lactide)-*block*-polyethylene (PLLA-*b*-PE). The orientation of both PLLA and PE crystals with respect to the lamellar interface was examined under two types of crystallization condition with a broad range of crystallization temperatures (T_c). The first type was the "two-stage crystallization", where the PLLA block was allowed to crystallize before PE. The second was the "one-stage crystallization", where PLLA and PE blocks competed to crystallize. A homeotropic crystal orientation was always observed for the PLLA crystals with the crystalline stems lying parallel to the lamellar normal regardless of the crystallization condition, except when T_c approached the glass transition temperature of PLLA where the orientation became random. On the other hand, a homogeneous crystal orientation with the PE crystalline stems oriented perpendicular to the lamellar normal was always identified at low to intermediate degree of undercooling, whereas at large undercooling the crystals showed random orientation. The novel "orthogonal orientation" disclosed here was preserved over a broad range of undercooling. Our results further demonstrated that the orientation of both PLLA and PE crystals depended mainly on T_c, but was independent of the competitiveness of the two crystallization processes. This was a consequence of the strong segregation that made the two blocks crystallize independently within their respective microdomains.

Molecular Characteristic and Thermal Properties

Copolymers	Volume fraction of PLA block	$\bar{M}_n$ (g /mol)		PE	T_{ODT}	T_m^{PLLA}	T_m^{PE}	T_g^{PLA}
		PLA block	PE block	% 1,2 Units	(°C)	(°C)	(°C)	(°C)
PLLA-PE	0.43	22500	26500	7.2	> 220	171.7	104.2	62.1
PDLLA-PE	0.47	32400	27700	7.0	> 220		103.5	55.0

Results and Discussion



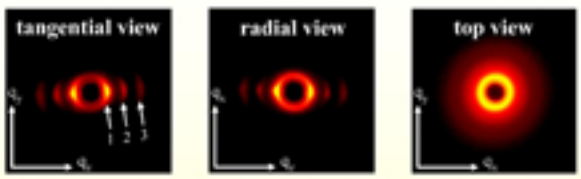


Figure 1. Schematic illustrations of the geometry of shear-oriented PLLA-*b*-PE specimen, indicating different incident directions of the X-ray for obtaining the 2-D scattering patterns in tangential-view (the X-ray beam is travelling along x), radial-view (the X-ray is along y) and top-view (the X-ray is along z).

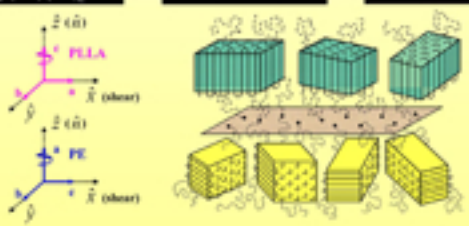


Figure 2. The 2D WAXD patterns of shear-oriented PLLA-*b*-PE subjected to a two-stage crystallization process. The system was cooled from 190 to 120 °C to allow for PLLA crystallization followed by cooling to T_c^{PE} = 97 °C to induce PE crystallization (similar results were also obtained for T_c^{PE} = 60 ~ 80 °C).

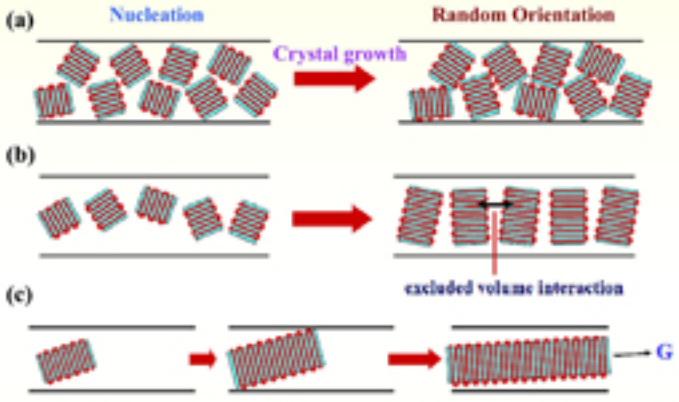


Figure 3. Schematic illustration showing the control of crystal orientation by the competition between nucleation and crystal growth kinetics. (a) At very large undercooling a large number of nuclei exploded in the microdomain almost simultaneously. The domain was quickly filled with randomly oriented nuclei and the jamming of these crystallites frustrated the crystal growth, thereby leading to random orientation eventually. (b) At lower undercooling the nucleation density was still quite high, but the crystal growth was operative in the domain. The growing lamellae-shaped crystallites experienced an excluded volume interaction to yield homogeneous orientation. (c) At low undercooling where the nucleation density was so low. The crystal would adjust its orientation to facilitate long-range growth and eventually adopted homeotropic orientation.

Conclusion

Sample / Temperature	PDLLA-*b*-PE	PLLA-*b*-PE			
	crystallization PE	sequential crystallization (two-stage)		competitive crystallization (one-stage)	
		PLLA	PE	PLLA	PE
97 °C	//	⊥	//	⊥	//
80 °C	//	⊥	//	⊥	//
70 °C	//	⊥	//	O	//
60 °C	//	⊥	//		//
45 °C	//	⊥	//		//
40 °C	//	⊥	//		//
30 °C	O	⊥	O		O
10 °C	O	⊥	O		O
-10 °C	O	⊥	O		O
-30 °C	O	⊥	O		O
-50 °C	O	⊥	O		O
Liquid N_2	O	⊥	O		O
Liquid N_2 reheat to 70 °C	O			O	O
Liquid N_2 reheat to 90 °C	O			⊥	O

Note: ⊥ denotes the homeotropic crystal orientation, where the c-axis orientation is parallel to lamellar normal; // signals the homogeneous crystal orientation, where the c-axis orientation is perpendicular to lamellar normal ; O indicates random orientation, where the c-axis orientation is randomly distributed with respect to lamellar normal.)