Supporting Information

Multifaceted Property Tailoring of Polyamide 6 by Blending Miscible and Immiscible components: Ternary Blends of Polyamide 6/Polyethylene Terephthalate/Phenol Novolac

Takayuki Hirai^{a,*}, Yusaku Onochi^b, Jumpei Kawada^a

^aMaterial and Processing Department, Polymer Processing and Mechanics Laboratories, Toyota

Central R&D Laboratories, Inc., 41-1 Yokomichi, Nagakute 480-1192, Japan

^bLightweight Material Development Group, Organic Material Dept., Organic Material Engineering

Div., Toyota Motor Corporation, Toyota-cho, Toyota, Aichi, Japan

*Corresponding Author. Email: hirai@mosk.tytlabs.co.jp

Abbreviations

PA6: Polyamide 6, PBT: poly(butylene terephthalate), PEN: poly(ethylene naphthalate), PEI: poly(ether imide), PN: phenol novolac



Figure S1. Temperature dependencies of (a) the storage modulus and (b) tan δ of PA6 in dry state after vacuum drying and water-absorbed state after reaching equivalent state in water. The water molecules act as a plasticizer and the glass transition temperature (T_g) of PA6 is low-temperature shifted by water absorption.



Figure S2. (a) Temperature dependencies of the storage modulus and (b) flexural moduli of PA/PET and ternary blends in water-absorbed state (PA6/PET/PN5:PA6/PET including 5 wt% PN and PA6/PET/PN15: including 15 wt% PN.)



Figure S3. (a) Viscoelastic behavior and (b) stress–strain curves of PA6 and the polymer blends, which were obtained from vacuum-dried specimens.



Figure S4. Viscoelastic behavior of homo PA6, homo PBT, and the polymer blends in waterabsorbed state. Temperature dependencies of (a) the storage modulus and (b) tan δ .



Figure S5. Viscoelastic behavior of homo PA6, homo PEN, and the polymer blends in waterabsorbed state. Temperature dependencies of (a) the storage modulus and (b) tan δ .



Figure S6. Scanning electron micrographs of the polymer blends. Compatibilization by PN loading is observed in both the PA6/PBT and PA6/PEN blends.



Figure S7. Viscoelastic behavior of homo PET and the PET/PEI blends. Temperature dependencies of (a) the storage modulus and (b) tan δ . PET/PEI blends present a single T_g and their miscibility is confirmed. Re-crystallization behavior is observed in all the specimens, owing to insufficient crystallinity of the prepared specimens.



Figure S8. Viscoelastic behavior of the homo PA6, PA6/PET/PN ternary blend, and PA6/PET/PN/PEI quaternary blend in water-absorbed state. Temperature dependencies of (a) the storage modulus and (b) tan δ .

EXPERIMENTAL

Sample Preparation

PA6/PBT Blends

Standard-grade PA6 (A1030BRL, Unitika, Japan), PBT (Duranex 2002, Polyplastics, Japan), and heat-resistant-grade PN (PAPS PN70, Asahi Yukizai, Japan) were employed in this study. All the polymers were vacuum-dried prior to melt mixing. Melt mixing was conducted using an internal mixer (Laboplastomill, Toyo Seiki, Japan) with a cylinder temperature of 250 °C, rotation speed of 100 rpm, and mixing time of 5 min. The sample designations and composition ratios of the prepared blends are listed in Table S1.

PA6/PEN Blends

Standard-grade PA6 (A1030BRL, Unitika, Japan), PEN (Teonex TN-8065S, Teijin Limited, Japan), and heat-resistant-grade PN (PAPS PN70, Asahi Yukizai, Japan) were employed in this study. All the polymers were vacuum-dried prior to melt mixing. Melt mixing was conducted using an internal mixer (Labo Plastomill, Toyo Seiki Seisaku-sho, Japan) with a cylinder temperature of 290 °C, rotation speed of 100 rpm, and mixing time of 5 min. The sample designations and composition ratios of the prepared blends are listed in Table S1.

PET/PEI Blends

Standard-grade PEI (Ultem 1000, Sabic, Saudi Arabia) and injection-molding-grade PET (TRN-0855FF, Teijin Limited, Japan) were employed in this study. All the polymers were vacuum-dried prior to melt mixing. Melt mixing was conducted using a micro compounder (HAAKE Minilab, Thermo Fisher Scientific, Germany) with a cylinder temperature of 270 °C, rotation speed of 200 rpm, and mixing time of 5 min. The sample designations and composition ratios of the prepared blends are listed in Table S1.

PA6/PET/PN/PEI Blend

Standard grade PA6 (A1030BRL, Unitika, Japan), PEI (Ultem 1000, Sabic, Saudi Arabia), injectionmolding grade PET (TRN-0855FF, Teijin Limited, Japan), and heat-resistant grade PN (PAPS PN70, Asahi Yukizai, Japan) were employed in this study. All polymers were vacuum-dried prior to melt mixing. Melt mixing was conducted using an internal mixer (Labo Plastomill, Toyo Seiki Seisakusho, Japan) with a cylinder temperature of 270 °C, rotation speed of 100 rpm, and mixing time of 5 min. The sample designations and composition ratios of the prepared blends are listed in Table 1.

Sample designation	PA6 (wt%)	PBT (wt%)	PEN (wt%)	PET (wt%)	PEI (wt%)	PN (wt%)
PA6/PBT	50	50				
PA6/PBT/PN10	45	45				10
PA6/PBT/PN20	40	40				20
PA6/PEN	50		50			
PA6/PEN/PN10	45		45			10
PA6/PEN/PN20	40		40			20
PET/PEI10	90				10	
PET/PEI20	80				20	
PET/PEI30	70				30	
PA6/PET/PN/PEI	40			40	10	10

Table S1. Sample designations and constituent weight fractions

Dynamic Mechanical Analysis (DMA) at Water-Absorbed State

The homo polymers and melt-mixed samples were melt-pressed into rectangular specimens (35 mm × 5 mm × 0.5 mm) using a laboratory press at temperatures of 250, 270, and 290 °C for the polymer blends comprising PBT, PET, and PEN, respectively. The specimens were cooled by a second laboratory press at 150 °C to promote crystallization of the specimens by slow cooling. The specimens listed in Figure S6 were vacuum-dried at 80 °C for 12 h prior to measurement. The other specimens were immersed in distilled water at 23 °C overnight before measurement. DMA was carried out using a dynamic mechanical analyzer (DVA-225, ITK, Japan) in the temperature range -100–200 °C with a heating rate of 5 °C/min and a frequency of 10 Hz.

Scanning Electron Microscopy (SEM)

The cryo-fractured surfaces of the polymer blends were fabricated by fracturing the rectangular specimens (50 mm × 10 mm × 2 mm) in liquid nitrogen. Each fractured surface was sputter-coated with platinum and observed by SEM (S-3600N, Hitachi, Japan) at an accelerating voltage of 15 kV.